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NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Chemistry of Cement

Proceedings of the
Fourth International Symposium
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Volume II

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Preface

Symposia on the chemistry of cements have become established through a succession of international assemblies held at irregular intervals. More than a half century ago such meetings among researchers, covering various materials including cements, were sponsored by the International Association for Testing Materials.

The first international congress dealing exclusively with the chemistry of cements and related materials seems to have been a meeting sponsored by the Faraday Society and held in London on January 14, 1918. Because of the priority of that meeting in this special field, it has come to be known as the First International Symposium on the Chemistry of Cement.

The First Symposium was designated as "A General Discussion" on "The Setting of Cements and Plasters." Ten brief papers were presented by 11 scientists from 5 countries. Twelve discussions followed the presentation of the papers. The Proceedings consisted of 69 pages published in the Transactions of the Faraday Society, Volume XIV, 1918–19.

The Second Symposium was sponsored by the Royal Swedish Institute for Engineering Research and the Swedish Cement Association. A 3-day meeting was held in Stockholm in July of 1938 under the designation "Symposium on the Chemistry of Cements." Forty-seven persons from 13 countries participated in the presentation of 13 papers and 52 discussions. The Proceedings, consisting of 578 pages, were published in Stockholm in 1939 by the Royal Swedish Institute for Engineering Research.

The intervention of World War II delayed consideration of the next symposium. Preliminary plans for a general meeting in Washington were abandoned, but eventually arrangements were made for the Third Symposium to be held in London under the sponsorship of the Department of Scientific and Industrial Research and the Cement and Concrete Association. The five-day meeting was held in September of 1952, and was attended by 260 persons, 84 of whom participated with 23 papers and 102 discussions. The Proceedings, consisting of 870 pages, were published in London in 1954 by the Cement and Concrete Association.

Preliminary conversations on the organization of the Fourth Symposium were initiated in April 1956, at which time agreement was reached by the National Bureau of Standards and the Portland Cement Association that the Symposium would be jointly sponsored by those organizations. By the spring of 1959 a tentative program had been set up with the cooperation of leaders in cement research of several foreign countries. Later in that year the organization of the working committees was completed. The sponsors and members of committees are listed below.

Sponsors: National Bureau of Standards, Allen V. Astin, Director; Portland Cement Association, G. Donald Kennedy, President.

Executive Committee: I. C. Schoonover, and A. Allan Bates, Cochairmen; R. H. Bogue, Secretary, Robert E. Pflaumer, Douglas E. Parsons, Myron A. Swayze, W. S. Weaver, C. E. Wuerpel, and Hubert Woods.

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Arrangements Committee: J. H. Walker and Bruce Foster, Cochairmen; Clayton Davis and William Lerch.

Editorial Committee: E. T. Carlson and H. H. Steinour, Cochairmen; E. S. Newman and M. D. Catton.

Papers for presentation at the Symposium were received at the Secretary's office, beginning in January 1960, and continuing to September. After review by the Program Committee and some preliminary editing by the Editorial Committee, they were reproduced by a photoduplicating process, and copies were mailed, as they became available, to the Symposium members.

The Fourth Symposium was held at Washington, D.C., October 2–7, 1960. Invitations to membership in the Symposium were accepted by 362 persons, including 169 from the United

States and 193 from 34 other countries. The number actually in attendance was 271. All sessions of the Symposium were held at the National Bureau of Standards.

At the first session, held on Monday morning, October 3, Dr. I. C. Schoonover, Associate Director of the National Bureau of Standards, and Dr. A. Allan Bates, Vice President of the Portland Cement Association, acted as cochairmen. Dr. A. T. McPherson, Associate Director of the National Bureau of Standards, welcomed the guests on behalf of the Bureau, and Mr. G. Donald Kennedy, President of the Portland Cement Association, indicated his pleasure in cosponsoring this important gathering. Dr. Eberhard Spohn, President of the Heidelberg Cement Company, responded on behalf of the members of the Symposium.

The first formal address, given by Dr. Wallace G. Brode, formerly Science Advisor to the Secretary of State, was entitled "Some Problems Associated with the Growth of Science." This was followed by an address, given by Dr. F. M. Lea, Director of the Building Research Station of the United Kingdom, entitled "Cement Research, Retrospect and Prospect."

Succeeding sessions were devoted to technical papers, grouped under seven general topics related to the chemistry of cement.

The titles of the individual papers will not be given here, as they are listed in the table of contents. The program included the following sessions.

Session II—Chemistry of Clinker; Monday afternoon, October 3; Dr. Henri Lafuma and Dr. R. H. Bogue, presiding.

Session III—Chemistry of Hydration of Cement Compounds; Tuesday morning, October 4; Dr. Fritz Keil and Mr. Charles E. Wuerpel, presiding.

Session IV—Chemistry of Hydration of Portland Cement; Tuesday afternoon, October 4; Dr. Niko Stutterheim and Mr. Myron A. Swayze, presiding.

Session V—Properties of Cement Paste and Concrete; Thursday morning, October 6; Dr. Wolfgang Czernin and Mr. Hubert Woods, presiding.

Session VI—Destructive Processes in Concrete; Thursday afternoon, October 6; Dr. Arturo Rio and Mr. Douglas E. Parsons, presiding.

Session VII—Chemical Additions and Admixtures—was combined with Session VIII.

Session VIII—Special Cements; Friday morning, October 7; Prof. B. G. Skramtaev and Dr. A. R. Collins, presiding.

The technical communications were of three categories, as follows:

1. Principal papers by outstanding contributors to the literature of cement and concrete technology, who were invited to present their appraisal of the present state of knowledge in their assigned topics;
2. supplementary papers submitted by members of the Symposium, presenting new and original research dealing with the specific topics of the Symposium, and
3. discussion of principal and supplementary papers, presented by members of the Symposium.

Papers were presented in condensed form, but are given in full in these Proceedings. Some of the discussions were submitted prior to the Symposium, others at the time of the meetings or subsequent thereto.

After the Symposium, authors were invited to submit corrections to their papers, but did not have opportunity to read printers' proof. Readers of the Proceedings are asked to make allowance for this, as well as for the facts that some papers are the joint product of authors and translators, and that translations had sometimes to be edited without access to the original manuscripts.

Following the sessions in Washington, many of the members of the Symposium accepted a general invitation to travel to Skokie, Ill., to visit the laboratories of the Portland Cement Association and to attend a series of seminars there. A two-day expense-paid bus trip from Washington to the vicinity of the laboratories was arranged by the Portland Cement Association for foreign guests to enable them to see the countryside and to observe some typical highway systems, expressways, toll roads, and city streets in the United States.

The program at Skokie, October 10–12, included seminars on cement manufacture and on basic and applied research, as well as laboratory tours and demonstrations.

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Explanatory Notes

Abbreviations. The following symbols, which have been widely adopted by cement chemists for formulating more complex compounds, are used interchangeably with the respective oxide formulas throughout this book: $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$, $M=MgO$, $N=Na_2O$, $K=K_2O$, $H=H_2O$. Less common abbreviations of this type are defined as they occur.

Commonly used abbreviations of more general nature include the following:

DTA=differential thermal analysis
FM=fineness modulus
IR=infrared
NMR=nuclear magnetic resonance
psi (or p.s.i.)=pounds per square inch
rh (or r.h.)=relative humidity
w/c (or W/C)=water-cement ratio

Identification Numbers of Papers. Each symposium paper has been assigned an identification number. Examples: Paper II–1 is the first principal paper of session II; paper II–S1 is the first supplementary paper of session II. With few exceptions, the numbers correspond to those assigned to the copies of the papers distributed in advance of the symposium.

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Proceedings of the Fourth International Symposium on the Chemistry of Cement

SESSION V. PROPERTIES OF CEMENT PASTE AND CONCRETE

Paper V–1. Physical Properties of Cement Paste*

T. C. Powers

Synopsis

This paper deals mainly with cement paste in terms of its porosity, internal surface area, interaction between solid substance and evaporable water and related properties. There are 10 sections as follows: (1) introduction; (2) properties of fresh paste; (3) specific volume of hydrated cement and porosity of paste; (4) surface area of hydrated cement, and indicated particle size; (5) minimum porosity of hydrated paste and specific volume of cement gel; (6) concepts of structure of cement gel and cement paste; (7) mechanical effects of adsorption and hydrostatic tension; (8) instability of cement paste; (9) strength; (10) permeability.

Among the subtopics are the following: definition of pore and solid; permeability of paste at all stages of hydration; measurement of surface area; specific volume of cement gel; computation of capillary porosity; physical aspects of hydration products; adsorption and capillary condensation; spontaneous decrease of specific surface area of hydrated cement; irreversible deformations; gel-space ratio vs. strength; theories of permeability; viscosity of water in cement paste; capillary continuity and discontinuity.

A glossary of terms is appended.

Résumé

Cet exposé traite principalement de la pâte de ciment en fonction de sa porosité, de la surface spécifique interne, de l'action réciproque entre la substance solide et l'eau évaporable, et des propriétés qui s'y rapportent. Il y a 10 sections qui sont les suivantes: (1) introduction; (2) propriétés de la pâte fraîche; (3) volume spécifique du ciment hydraté et porosité de la pâte; (4) surface spécifique du ciment hydraté, et indication sur la taille des particules; (5) porosité minimum de la pâte hydratée et volume spécifique du gel de ciment; (6) concepts de structure du gel de ciment et de la pâte de ciment; (7) effets mécaniques de l'adsorption et de la tension hydrostatique; (8) instabilité de la pâte de ciment; (9) résistance; (10) perméabilité.

Parmi les points secondaires, les suivants sont traités: définition de pore et de solide; perméabilité de la pâte à tous les stades de l'hydratation; mesure de la surface spécifique; volume spécifique du gel de ciment; calcul de la porosité capillaire; aspects physiques des produits d'hydratation; adsorption et condensation capillaire; diminution spontanée de la surface spécifique du ciment hydraté; déformations irréversibles; rapport gel-espace versus résistance; théories de perméabilité; viscosité de l'eau dans la pâte de ciment; continuité et discontinuité capillaires.

Un lexique des termes se trouve en appendice.

Zusammenfassung

In dem Vortrag werden hauptsächlich die Porosität, die Größe der inneren Oberfläche, die Reaktion zwischen festem Körper und verdampfbarem Wasser und die damit zusammenhängenden Eigenschaften der Zementpasten beschrieben. Die zehn Kapitel haben die folgenden Überschriften: (1) Einleitung; (2) Eigenschaften der frischen Paste; (3) Das spezifische Volumen des hydratisierten Zementes und die Pastenporosität; (4) Oberfläche des hydratisierten Zementes und wahrscheinliche Teilchengröße; (5) Die Minimumporosität der hydratisierten Paste und das spezifische Volumen des Zementgels; (6) Der Zementgel- und Zementpastenstrukturbegriff; (7) Mechanische Effekte der Adsorption und der hydrostatischen Spannung; (8) Unbeständigkeit der Zementpasten; (9) Festigkeit; (10) Permeabilität.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Illinois.

Als sekundäre Themen behandelt sind: Definition der Pore und des festen Körpers; Pastenpermeabilität in allen Hydratationsstufen; Oberflächenmessung; Das spezifische Volumen des Zementgels; Berechnung der kapillären Porosität; Physikalische Eigenschaften der Hydratationsprodukte; Adsorption und Kapillarkondensation; Abnahme der spezifischen Oberfläche des hydratisierten Zementes; Nicht umkehrbare Formveränderung; Die Festigkeit als eine Function des Verhältnisses gel/space; Permeabilitätstheorien; Die Viskosität des Wassers in der Zementpaste; Kapilläre Stetigkeit und Unstetigkeit.

Eine Liste der benutzten Worte ist am Ende hinzugefügt.

1. Introduction

The chemical origins of the substance called cement paste, and the physico-chemical processes of its formation, are essential elements of the study of physical properties of cement paste, and the properties of cement paste are reflected in almost every aspect of concrete technology. Thus, the study of cement paste provides a bridge between cement chemistry and concrete technology. A subject of such broad scope involves the whole literature of cement and concrete, and a complete critical review would have required more time than was available. Therefore, a complete review was not attempted.

This review turned out to be an occasion for revision and reassessment of our own work, and this entailed introducing some material not published before. Concepts of structure have been emphasized, and special attention is paid to a few points that have proved to be somewhat controversial. Perhaps the most important of these is the question of internal surface area: Are internal surfaces real, and have we measured them?

Little is said about differences in the chemical compositions of cements because the physical properties of paste are not much influenced by such differences. Any hydrated portland cement is predominantly colloidal and this point of similarity outweighs the points of difference attributable to differences in chemistry.

The words used for describing hydrated cement are those required for describing a chemically unidentified substance. In 1947 it was not possible, and still in 1960 it is not feasible, to use much chemical nomenclature. The ratios $CaO:SiO_2:H_2O$ for substances in cement paste are not definitely established, to say nothing of other components. There is reason to suspect that unique molecular ratios are not characteristic of hydrated cements. So, in this 1960 review it is still necessary to refer to grams of "nonevaporable water", and to "hydrated cement", instead of conventionally designated molecular species. The result is rather unsatisfactory to chemists and nonchemists alike, since a discussion based on arbitrary special definitions often becomes confusing if those definitions are overlooked. (A glossary of terms will be found in appendix 1.) Possibly, after other papers of this symposium have been digested, terminology will be improved.

2. Properties of Fresh Paste

The Dormant Period

During a short period beginning at the time of contact between cement and water, relatively rapid chemical reactions occur. Then follows a longer period of low activity which has been called the dormant period. [1, 2].[1] It is the time during which paste normally remains plastic, and, at room temperature, it normally lasts 40 to 120 min, depending on the characteristics of the cement.

The initial reaction does not seem to alter the size and shape of the cement grains very much. This is indicated, for example, by the following data obtained with a Wagner turbidimeter by Ernsberger and France [3].

Material	Dispersion medium	Specific surface cm²/g
Cement A	Kerosene	1, 690
Cement A	Water	1, 705
Cement B	Kerosene	2, 590
Cement B	Water	2, 630

Powers [4] found that the specific surface area calculated from the rate of bleeding of cement pastes by a modified Kozeny-Carman equation, was about the same for a paste made with kerosene as with water. Steinour [5] measured the bleeding rates of one cement in various liquids. The values for specific surface area, calculated from the Kozeny-Carman equation [6] were as follows:

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[1] Figures in brackets indicate the literature references at the end of this paper.

Name of liquid	Surface area, cm²/g
Dioxane	1, 680
Hexyl ether	1, 630
Butyl alcohol	1, 670
Octyl alcohol	1, 680
Diethylphthalate	1, 675
Average	1, 670
Water	1, 710

These figures indicate that reaction with water caused a slight increase in specific surface area.

The constancy of the rate of bleeding during the dormant period shows that the new products formed by reactions occurring during the dormant period do not effectively alter the surface contours of the particles, or change the viscosity of the liquid. Possibly, the layer of hydration products first formed, around which water flows during bleeding, is of loose enough texture to accommodate the small quantity of material produced during the dormant period.

Preparation of Pastes

The physical characteristics of a batch of fresh paste depend on how the paste is prepared. When mixed by gentle stirring, the paste remains stiff relative to the consistency produced by vigorous mechanical stirring [7]. Dry cement, which is normally in a flocculated state, is apparently not uniformly dispersed by wetting alone. To produce a homogeneous paste of lowest possible stiffness, a laboratory mixer able to produce a high rate of shear is necessary.

Length of mixing period is important. If it is of the order 30 sec or less, the paste becomes firm soon after mixing stops [8]. Steinour called this phenomenon "brief-mix-set" and attributed it to the grains becoming stuck together by gel in process of forming on grain surfaces. Even if the mixing period is long enough to prevent brief-mix-set, which is usually the case, it may be too short to eliminate false set. In the laboratory, it is advisable to allow a period of rest between an initial and final mixing period, the length of the rest period having been determined by trial for each cement. Examples of mixing schedules required to eliminate false set are given in table 1.

With the exception of matters pertaining to false set, time effects and mixing procedures are principally laboratory problems. Under normal field conditions, the time of mixing can hardly be so short as to permit brief-mix-set, and the rolling mass of aggregate in a concrete mixer "homogenizes" the paste as effectively as the most vigorous laboratory stirrer.

When a paste is properly prepared, its properties are reproducible, and are amenable to quantitative study. A considerable amount of such study has been done, and it gave information about the structure of fresh paste that is not only essential to an understanding of the properties and behavior of fresh concrete, but also is pertinent to various aspects of mature concrete.

TABLE 1. *Mixing schedules required by different cements to eliminate false set*

Specific surface: 1,500 cm²/g (Wagner Turbidimeter)

Tests were on 1:2 (by wt.) mortars made with Elgin sand.

w/c is that required for (1±0.05)-inch slump, with 6-in cone, after a 1 min mix

The first number of the mixing schedule is the length of the first period o mixing; the second is the period of rest; the last is the final mixing period.

ASTM type	Lot No.	w/c by wt.	Condition after 1-min mix		Required mixing schedule	Remolding effort, jigs	Slump 6-in. cone
			R.E. [c]	Slump			
					min		*in*
1	15753	0. 36	27	1. 05	2–0–0	25	1. 25
1	15760 [b]	. 35	41	. 85	2–2–2	33	1. 10
2	15755 [a]	. 34	32	1. 10	2–2–2	26	1. 10
3	15757 [a]	. 34	33	. 95	2–3–2	27	1. 05
4	15762 [b]	. 34	42	. 85	2–5–2	22	1. 40

[a] This cement showed evidence of moderate false set.
[b] This cement showed marked false set.
[c] Remolding effort, number of jigs.

The Flocculent State

During the dormant period, properly prepared paste is a thick suspension of particles in a flocculent state. Steinour [9] found that the term "flocculent state" is not to be construed to mean that the paste consists of a collection of more or less separate floccules. Instead, the whole body of paste constitutes a single floc, the floc structure being a rather uniform reticulum of cement particles. Because of such structure, fresh paste has some cohesive strength, as shown by its rheological properties.

The flocculent state can be modified or destroyed by means of surface-active agents. Such agents have been studied extensively, particularly in the Soviet Union, but, this being the subject of another paper of the Symposium, it will not be dealt with here.

Studies of sedimentation volume indicate that cement particles in water, though flocculent, are not normally far from the dispersed (nonflocculent) state [10]. The sedimentation volume of cement in dry alcohol, in which the particles are completely dispersed, is only a little smaller than the sedimentation volume of cement particles in water, whereas the sedimentation volume in a nonpolar liquid, benzene, for example, is nearly twice that in dry alcohol. The relatively low intensity of interparticle attraction between cement particles in water is probably due to the hydrophilic nature of cement.

Although the floc structure of cement paste has some strength and rigidity, the cement particles are nevertheless discrete during the dormant period. This was shown by measurements of hydrostatic pressure [11]. The constancy of the rate of bleeding also shows that the particles remain discrete during the dormant period. It appears that where the gel-coated grains are almost in contact, they are separated by a thin layer of water, probably only a few angstrom units thick. The constancy of the bleeding rate signifies in particular that such thin, separating layers of water have no solidity.

This last-mentioned observation seems contrary to what has been reported for some mixtures of clay and water [12], namely, that rigid, ice-like structures develop in the small spaces between solid surfaces. The flocculent state in cement paste seems explicable in terms of classical theory, viz., the gel-coated grains carry a "solvated layer" and they have a positive zeta potential [13]. The combined effect of solvated layer and electrostatic charge is such as to prevent actual contact between adjacent grains. But the grains are concentrated enough to experience interparticle attraction, at least over parts of their boundaries. The effects of repulsion and attraction balance at a certain distance of separation where the potential energy of the particles is at a minimum. The cement grains tend to remain in "potential troughs", which are so located as to require spaces between the particles.

Solvated surfaces and electrostatic charge account in part for the kind of rheological properties exhibited by cement pastes. Other factors are the size, shape, and concentration of particles, and the viscosity of the fluid. In pastes of relatively stiff consistency, effects of interparticle forces dominate, viscosity playing a minor role [14]. At softer consistencies, w/c=0.4 and above, cement paste is, as Reiner puts it, " . . . a first approximation to a Bingham body" [15].

Sedimentation (Bleeding)

Because cement particles remain discrete during the dormant period, and because the suspending medium is viscous, the suspension is not stable under the pull of gravity; cement paste "bleeds". Bleeding has been referred to as an aspect of coacervation [16] but experimental evidence that it is something other than gravitational settlement seems lacking.

The initial rate of bleeding remains constant for a period determined by various factors [1, 2]. Although the largest cement particles are a hundred or more times the size of the smallest, all sizes are forced to fall at the same rate because of the flocculent state. Hence, the fluid appearing above the solids remains clear and free from fine particles. If sedimentation becomes completed within the dormant period, physical factors alone determine the particle concentration in the final sediment. When setting arrests bleeding before the process is physically complete, the final sediment does not have uniform concentration of cement grains. At the bottom there may be a layer of completed "sedimentation zone", but, at the top, w/c remains at the initial value. Thus, the final composition of a specimen of cement paste may differ from the initial composition, and the specimen as a whole may become considerably less homogeneous than it was at the beginning.

The lowest possible water content of the completed sediment is higher, the higher the original water content of the paste [18]. In contrast to this, Steinour found that thick suspensions of emery would always settle to the same final volume, regardless of the initial volume of the suspension, provided the particles were in a nonflocculent state [19]. Presumably, cement particles would do the same were it not for their flocculent state.

The greatest possible amount of water that can be lost from a paste by bleeding under the force of gravity alone has been called the "bleeding capacity" [18]. It is a function of the initial water content, and it appears to follow a regular law. Steinour's studies led to several approximations of it, one of which may be stated as follows:

$$\Delta H' = \frac{K^2 c \rho_c}{V} [w/c - (w/c)_m]^2. \qquad (1)$$

Where $\Delta H'$ is the bleeding capacity expressed as settlement per unit of original height; w is the initial weight of water; c the weight of cement; ρ_c is the density of the cement, and V is the initial volume of the paste. The symbols K, and $(w/c)_m$, are empirical constants characteristic of a given cement, and are dependent mostly on the surface area of the cement; $(w/c)_m$ was interpreted as the water cement ratio of a "base" paste in which the particles are so concentrated that bleeding cannot occur. It is evaluated by extrapolation of plotted data, and may be regarded as referring to a hypothetical paste.

The values of the constants in eq (1), for a given cement, can be altered by any means that changes the state of flocculation. Increase of interparticle attraction increases the base water content, and vice versa. Owing, presumably, to the interparticle water films, the base volume is larger the finer the cement.

Permeability of Fresh Paste

Rate of bleeding is related to the coefficient of permeability of the (nonsettled) paste as shown in eq (2).

$$Q = K_1[(\rho_c/\rho_f) - 1](1 - \epsilon). \qquad (2)$$

Q is the rate of bleeding in cm/sec, or cc/cm^2 sec; K_1 is the coefficient of permeability to a specific fluid at a specific temperature, in cm/sec; ρ_c and ρ_f are densities of cement and fluid respectively, in g/cc; ϵ is the volume of fluid-filled space per unit volume of paste, i.e., the porosity.

The permeability of paste made with a given cement depends on temperature and water content. There is a limiting water content below which the pastes all maintain continuous floc structure during bleeding, and above which the structure becomes ruptured and "channeled bleeding" occurs [20]. Most of the ensuing discussion pertains to "normal" rather than "channeled" bleeding.

The mean size of pores in fresh paste can be estimated from hydraulic radius, that is, the quotient of water content and wetted surface area. An example is given in table 2. The figures in the final column are based on the assumption that the section of a typical pore resembles a rectangular slit [21]. At a given water content the pore size is smaller the larger the specific surface area of the cement.

TABLE 2. *"Pore" sizes of fresh pastes for cement having a surface area of 6,000 cm²/cc (1,900 cm²/g, Wagner)*

Water cement ratio by wt.	ϵ	Hydraulic radius, microns	Estimated average width of pore, microns
0.25	0.44	1.25	Between 2½ and 5
.40	.56	2.12	Between 4 and 8
.50	.61	2.60	Between 5 and 10
.60	.66	3.23	Between 6½ and 13
.70	.69	3.70	Between 7½ and 15

A theoretical equation for the coefficient of permeability making use of the hydraulic radius, and based on the Kozeny-Carman concept, is

$$K_1=\frac{\rho_f g}{k_0(\rho_c\Sigma)^2(1-w_i)}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)^2}. \tag{3}$$

The corresponding equation for bleeding rate is

$$Q=\frac{(\rho_c-\rho_f)g}{k_0\eta(\rho_c\Sigma)^2(1-w_i)}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)}. \tag{4}$$

Symbols not already used are defined as follows: Σ is the specific surface of the cement grains in cm²/g, as determined by a suitable permeability method; η is the viscosity of the fluid in poises. Theoretically, w_i is related to a fraction of the fluid that remains with the particles during flow. As shown by Steinour's work [22], the term $(1-w_i)$ of eq (4) must be squared when a specific surface value is used that is based on sedimentation analysis and calculated by Stokes' law in the usual way, which does not take account of fluid that accompanies the particles. The w_i seems to be composed of three elements, that is,

$$w_i=\frac{a+b\Sigma}{1+a+b\Sigma}+c \tag{5}$$

where $a(1-\epsilon)$ is a quantity of fluid held stagnant on the irregular grains, and $b\Sigma(1-\epsilon)$ is a volume added to the original cement grains by the initial chemical reaction. The terms a and $b\Sigma$ therefore occur because of an augmentation of the solids, and a diminution of the fluid, so far as flow is concerned. The c in w_i is zero for nonflocculated suspensions, but always appears when a thick suspension becomes flocculated. For spherical particles, $c=0.1$, approximately [23], and a and b are zero. For crushed glass, b is zero and w_i is approximately 0.18. Experiments with pulverized silica in suspensions of lime water with different concentrations of calcium hydroxide showed that as long as the floc structure was strong enough to give normal bleeding, varying the degree of flocculation did not influence c [24]. (The degree of flocculation does, however, strongly influence the bleeding capacity.) Steinour's data on experiments with suspensions of monodisperse emery particles showed that the change from nonflocculated to flocculated state simply increased w_i. Thus c represents the effect of flocculation per se. Perhaps the best explanation of it is that it represents water in isolated pockets excluded from the continuous floc structure, and is therefore not to be considered when computing the hydraulic radius of the floc structure.

The experimentally observed fact that the modified Kozeny-Carman equation represents experimental results accurately indicates that the product $k_0(1-w_i)$ is a constant that can be identified with the Kozeny-Carman constant, k. Thus

$$k=k_0(1-w_i). \tag{6}$$

Steinour's findings, expressed in terms of eq (6), but with $(1-w_i)$ squared since w_i was determined by sedimentation analysis, show that for suspensions of chemically inert spheres, w_i is zero and $k_0=4.06$. Such a value for spheres is in agreement with Carman's statement to the effect that k for fluidized spheres is equal to 4.0 [25]. If the particles are irregular but chemically inert, the a in w_i is finite and b is zero. In this case $k<4.06$. Obviously, if a and b are both finite, k may be still smaller.

Empirically, it was found that the bleeding rates of pastes conformed to eq (7) [26].

$$Q=\frac{(\rho_c-\rho_f)g}{5\eta(\rho_c s)^2}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)}. \tag{7}$$

In this equation s is the specific surface area as determined according to ASTM designation C 115–58. The constant 5 is correct only if this measure of surface area is used. The w_i factor must be evaluated empirically for each different cement by methods that have been described [27]. Steinour showed that variation in w_i among different cements was due principally to differences in specific surface and in the initial chemical reactions with water [28].

Capillary Forces in Cement Paste

The bleeding rate of concrete is of the same order of magnitude as the natural rate of evaporation from an open surface. Sun and wind together often cause the rate of evaporation to exceed the rate of bleeding. When this occurs, the surface loses its sheen, signifying that the plane surface of water has become replaced by myriad curved surfaces, and this signifies that capillary tension has been produced. Carman has shown that the maximum possible capillary tension in a water-filled granular bed occurs just as the water level drops below the upper boundary of the bed, and the meniscuses take on the greatest possible curvature, that being limited by the sizes and shapes of the spaces between particles at the top surface [29]. The approximate value of maximum capillary tension can be calculated from the following relationship adapted from the basic relationships given by Carman.

$$P_C = -\frac{\lambda\sigma\rho_f/\rho_c}{w/c} \tag{8}$$

where λ is the surface tension of water in dynes/cm, σ is the specific surface area of the cement in cm^2/cc, and P_C is capillary pressure, a negative quantity. Substitution of appropriate figures into eq (8) shows that maximum capillary tension will range from about ½ atm upwards depending on the surface area of the cement.

The reaction to capillary tension is, of course, an equal downward force exerted on the particles at the top of the bed. Since the downward force on those particles due to gravitation only is only about 0.001 atm, it is clear that when the rate of evaporation exceeds the normal rate of bleeding the force causing subsidence of the surface may be greatly increased. The effects of such an increase have been measured under controlled conditions by Klieger [30].

When resistance to consolidation becomes high enough to offset capillary tension, the water surfaces retreat to the interior, and lateral consolidation begins. The result is the so-called "plastic shrinkage", often giving rise to "plastic-shrinkage cracking". Swayze has expressed the view that a significant and technically important degree of compaction of fresh concrete can be produced by capillary tensions that may develop throughout a period of several hours, and he proposed a procedure for taking advantage of it [3].

3. The Specific Volume of Hydrated Cement and the Porosity of Hardened Cement Paste

Definition of Pore and Solid

It is undisputed that porosity is a basic property of hardened cement paste, but there may be disagreement as to the definition of pores. In the studies now being reviewed, pores are defined as spaces that can be occupied by water that is evaporable at a constant low external humidity, at a given temperature.[2] A change of either the specified temperature or humidity results in a corresponding change in the apparent ratio of solid to void. Thus, the choice of drying conditions defines the pore space and the solids, and does not assuredly isolate, or precisely establish, the true extent of the solid phases.

Problems of Mensuration

Besides the difficulty of isolating the solid phases, except on an arbitrary basis, the quantitative, accurate measurement of solid volume also presents difficult problems. Hydrated cement is mostly colloidal (see glossary) and of the total number of molecules composing the colloidal part, perhaps one-half to two-thirds of them are exposed at surfaces. Seen on an atomic scale, the surfaces of the particles, i.e., the boundaries of the pores, are transition zones of vibrating atoms, and thus the word surface as applied here does not connote the conventional geometric concept; the boundary is neither sharp, smooth, nor static. In regions of minimum porosity (see sections 5 and 6) the average distance between surfaces is about 5 oxygen-atom diameters, and in these places the rough transition region might constitute a significant fraction of the interparticle space.

The porosity of a given specimen is determined to a small but significant degree by the balance between opposing internal forces. To introduce a fluid into such a system of particles releases energy and alters the balance of forces. The surfaces change their relative positions, and the porosity changes too; swelling occurs. (See section 7). Even the specific gravity of the solid material may change slightly, owing to the change in interfacial free energy. The quantity of fluid that can be accommodated in interstitial spaces thus depends partly on the amount of swelling, accompanying entry of the fluid. It may depend, too, on how the molecules of the fluid "fit" the atomic roughness of the surfaces, and on the size of molecule relative to the size of the smallest interstitial spaces. Swelling produced by water is much greater than that produced by organic liquids or inert gases, water molecules being relatively small and strongly attracted by the surface.

Fluids that affect interparticle forces are themselves affected; they are adsorbed. Possibly, strongly adsorbed water molecules penetrate the transition region of the solid more than weakly absorbed molecules do. It is frequently suggested that some of the space found by sorbed water molecules is inside the crystals, but this seems doubtful, as will be seen further on. Whether or not these phenomena occur, it is probable that the average amount of space required per molecule of water in the adsorbed state is different from that required in the liquid state, which is to say that the average density of water in the adsorbed state may differ from that in the liquid state. Powers and Brownyard [32] estimated the specific volume of gel water, most of which is strongly adsorbed, at 0.90 cc/g. But this estimate was based on density of hydrated cement as determined by displacement in helium, and therefore it may not be correct for water, as was acknowledged at the time. Thus, although it is easy to determine the mass of water required to saturate the spaces in cement paste, it is impossible at present to determine a corresponding volume exactly.

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[2] This definition is not intended to include entrained air bubbles and the like, which are regarded as cavities rather than integral parts of paste.

Experimental Results

A direct approach to the problem of measuring porosity was based on the following expressions:

$$\epsilon=1-\frac{cv_c}{V}\left[1-m+m(1+w_n^\circ/c)\,\frac{v_{hc}}{v_c}\right] \tag{9}$$

$$\epsilon=1-\frac{m\left[(1+w_n^\circ/c)\,\frac{v_{hc}}{v_c}-1\right]+1}{1+\frac{w_0/c}{v_c}}. \tag{10}$$

ϵ is the porosity; m is the maturity factor (fraction of the original cement that has become hydrated); v_{hc} is the specific volume of hydrated cement in cc/g; w_n° is the nonevaporable water content of completely hydrated cement in grams; w_0 is the original water content in grams, corrected for water displaced by bleeding; c is the original cement content in grams, and v_c is the specific volume of the original cement in cc/g.

All the factors in eqs (9) and (10) are subject to direct measurement, but with attendant difficulties, especially for v_{hc}. In attempts to measure v_{hc}, various liquids were used as displacement media with various results [33]. For example, water, acetone, toluene, and helium gave the following values for v_{hc}, based on the normal density of each fluid: 0.395, 0.408, 0.429, and 0.424. These results from preliminary experiments were followed by a considerable amount of work with helium. The displacement in helium of samples prepared by the magnesium perchlorate method was finally reported, from work by Steinour [34], as 0.41 ± 0.01 cc/g for four different cements. Since the four cements were chemically different, and showed similarity in specific volume of hydration products, it was assumed that for any cement the approximate density of hydrated cement might be estimated from the relationship given in eq (11).

$$v_{hc}=\frac{v_c+v_n w_n^\circ/c}{1+w_n^\circ/c} \tag{11}$$

where v_n is the apparent specific volume of the nonevaporable water, cc/g. The values of v_n for the four cements were calculated from their helium displacements by means of eq (12).

$$v_n=\frac{(V_s/c)-v_c}{w_n/c}. \tag{12}$$

V_s is the volume of the dry sample, indicated by its displacement of helium, and c the cement content of the sample, grams. The mean value obtained for four different portland cements was $v_n=0.82$. The individual values ranged from 0.81 to 0.83.

An advantage of eqs (11) and (12) is that they permit evaluation of v_{hc} from gas displacement data on samples of paste that contain unhydrated cement.

Weir, Hunt, and Blaine [35] evaluated v_n from experiments based on eq (13).

$$v_s=v_c+(v_n-v_c)\,\frac{w_n/c}{1+w_n/c}. \tag{13}$$

In this equation, v_s is the specific volume of the solid material in the sample, cc/g, including unhydrated cement, if any. Small cylinders (½ x 4 in) of cement paste were cured for various periods and then dried by the "dry-ice" method of Copeland and Hayes [36]. Then the specimens were immersed in a light petroleum distillate, and the distillate and the specimen immersed in it were subjected to pressures up to 10,000 atm, the primary purpose of the experiment being to determine the compressibility of the solid phases. After release of pressure, the amount of distillate remaining in the specimen at atmospheric pressure was determined. Also the overall volume of the distillate-saturated specimen was measured by displacement. The resulting values of v_s were plotted against $(w_n/c)/(1+w_n/c)$, producing a straight line having an intercept at $v_s=v_c$. The slope of the line and the corresponding value of v_c gives, for a portland cement, $v_n=0.87$, for an aluminous cement, $v_n=0.75$. Comparing the result for portland cement with that reported by Powers and Brownyard, 0.82, Weir, Hunt, and Blaine mentioned that their higher result might be due to the presence of a little evaporable water in their specimens, because of incomplete drying. However, calculation shows that even if the specific volume of the residue of evaporable water in their specimens was as high as 1.0, the amount would have had to be about 40 percent of w_n, to account for the difference in question. Therefore, the data seem to indicate that helium penetrates regions not accessible to the distillate molecules.

The problem of determining the specific volume of hydrated cement and the specific volume of evaporable water has been approached by considering a saturated paste to be composed of two components: (1) the solid material and (2) the evaporable water [37]. From a normal procedure of physical chemistry, it follows that,

$$v_p'=N_{hc}'\bar{v}_{hc}+N_e'\bar{v}_e \tag{14}$$

in which v_p' is the specific volume of the paste, corrected for any residue of anhydrous cement; N_{hc}' is the weight fraction of hydrated cement; N_e' is the corresponding weight fraction of evaporable water; $\bar{v}_{hc}$ and $\bar{v}_e$ are the "partial specific volumes" of the solid material and evaporable water respectively. For example,

$$\bar{v}_e=\frac{\partial V}{\partial w_e} \qquad (15)$$

where V is the volume of the paste and w_e is the weight fraction of evaporable water. As used in the present case, $\bar{v}_e$ pertains to the evaporable water in a saturated specimen.

Among the many test data, the values of N'_e varied widely. When the values of specific volume of the specimen, v'_p cc/g, were plotted against corresponding values of N'_e, the points conformed closely to the straight line represented by the following equation.

$$v'_p=0.398N'_{hc}+0.99N'_e. \qquad (16)$$

Equation (16) seems to indicate that 0.398 is the specific volume of hydrated cement, and 0.99 is that of the evaporable water. However, a linear relationship such as eq (16) is characteristic of physical mixtures of two components that do not interact either chemically or physically when they are brought together. In the present case it is known that when dry hydrated cement and water are brought together the energy content of the system decreases, as shown by evolution of heat, the amount of heat released being over 20 cal/g of hydrated cement [38]. In view of this, it does not seem likely that the specific volume of either component would be the same after mixing as it was before. The following considerations seem to reconcile the result indicated by eq (16) and the observations just mentioned.

It is known that at humidities up to about 45 percent, the amount of water held in the adsorbed state is proportional to the amount of hydrated cement in the sample, and is independent of the total capacity for evaporable water. The amount adsorbed at 45 percent humidity is a little less than two molecular layers on the solid surface. This is the strongly adsorbed part of the evaporable water, as shown by its relatively high heat of adsorption. The rest comprises weakly adsorbed water and, if any, water free from the effects of adsorption. The fraction of the total evaporable water in excess of two molecular layers is greater the higher the porosity of the paste, and thus that part does not bear a constant ratio to the amount of hydrated cement.

It follows that if a specimen of saturated cement paste is to be treated as a two-component system, it is not permissible, a priori, to identify hydrated cement as one of the components, and total evaporable water as the other, because the properties of some of the evaporable water are certainly not independent of the other component, hydrated cement, although the properties of the rest of the water might be. It seems therefore that the simplest permissible assumption is that saturated cement paste is made up of three components: hydrated cement, adsorbed water, free water. On this assumption one would write in place of eq (14),

$$v'_p=N'_{hc}\bar{v}_{hc}+N'_a\bar{v}_a+(N'_e-N'_a)v_w \qquad (17)$$

where N'_a is the weight fraction of adsorbed water that stands in constant ratio to N'_{hc}, $\bar{v}_a$ is its partial specific volume and v_w is the specific volume of free water. Expressing the proportionality between adsorbed water and the solid material as $N'_a=bN'_{hc}$, and thereby eliminating N'_a from eq (17), we obtain

$$v'_p=N'_{hc}[\bar{v}_{hc}+b(\bar{v}_a-v_w)]+N'_e v_w. \qquad (18)$$

On comparing eq (18) with eq (16), we see that $v_w=0.99$ and $v_{hc}+b(\bar{v}_a-v_w)=0.398$. Therefore, the results obtained from this analysis were:

The linearity of the plot signifies either of two conclusions: (A) *All* the evaporable water has a specific volume of 0.99 cc/g (for these particular specimens) whether adsorbed strongly, weakly, or not at all, in which case $v_{hc}=0.398$, or (B) *Some* of the evaporable water in every specimen has a specific volume of 0.99, and the rest, an amount proportional to the amount of hydrated cement, might have a different specific volume, in which case the specific volume of the hydrated cement is not 0.398 cc/g. Conclusion (B) is probably the correct one.

Another analysis [37] was based on the empirical relationship

$$v_t=0.99-0.25\ w_n/w_t \qquad (19)$$

where v_t is the apparent specific volume of all the water in saturated specimens, including w_n. It would appear that at $w_n/w_t=1.0$, $v_t=v_n=0.74$, for, if eq (19) is valid over its entire range, the 0.25 is $\bar{v}_e-v_n$. However, on the basis of the same observations and reasoning presented in connection with eqs (16), (17), and (18), $(\bar{v}_e-v_n)w_n$ may be replaced by $(1+B)(v_w-v_d)w_n$, where B is the weight fraction of evaporable water that stands in constant ratio to w_n, and which may have a specific volume different from that of the rest of the evaporable water, and v_d is the mean of the specific volumes of the nonevaporable water and the part of the evaporable water whose density is altered by adsorption. Then

$$v_t=v_w-(1+B)(v_w-v_d)(w_n/w_t). \qquad (20)$$

On comparing eqs (19) and (20) it is evident that $(1+B)(0.99-v_d)=0.25$, or, $v_d=0.99-\frac{0.25}{1+B}$.

This result presents the same impasse as eq (18). It cannot be solved unless the fraction, B, of evaporable water having density different from that of the rest is known. Indeed, even if B were known, the apparent volume of the water in the solid phase, v_n, would still be unknown unless the mean density of the adsorbed water were known also. Only if it is arbitrarily assumed that $B=0$

Table 3. *Specific volume of hydrated cement*

$$v_{hc}=\frac{v_c+v_n\frac{w_n^\circ}{c}}{1+\frac{w_n^\circ}{c}}$$

v_{hc}=specific volume of hydrated cement
v_c=specific volume of original cement
v_n=apparent specific volume of nonevaporable water
$\frac{w_n^\circ}{c}$ =grams of nonevaporable water per g cement at complete hydration

Cement No.	Computed composition—%					v_c cc/g	$\frac{w_n^\circ}{c}$	v_{hc}, cc/g		
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$			$v_n=0.74$	$v_n=0.82$	$v_n=0.87$
15754	45.0	27.7	13.4	6.7	4.0	0.319	0.246 [a]	-----	0.418 [b]	-----
15754	45.0	27.7	13.4	6.7	4.0	.319	.227	0.397	.411	0.421
15622	49.2	28.5	4.4	12.8	2.7	.310	.176	.374	.386	.394
15699	33.0	54.2	2.3	5.8	3.1	.311	.174	.374	.386	.394
15497	60.1	11.9	10.3	7.9	3.1	.322	.210	.394	.408	.417

[a] This figure is based on samples prepared by the magnesium perchlorate method. All the rest in this column are for samples prepared by the dry ice method.
[b] This figure is on the magnesium perchlorate basis. All the others in the last three columns are on the dry ice basis, and are subject to limitations mentioned in the text.

and thus that $v_d=v_n$, do we obtain $v_n=0.74$. This is the lowest possible value for v_n.

Table 3 is a summary of the findings in terms of experimental and calculated results for four different cements. Specific volume as given in the first line corresponds to direct determinations by helium displacement of samples prepared by the magnesium perchlorate method. The rest of the values in the last three columns were calculated from the values of v_n at the heads of the columns. Values in the column headed $v_n=0.74$ are based on displacement in water (aqueous solution), and are the smallest possible, entailing the assumption that all parts of evaporable water have a specific volume of 0.99 cc/g. Values reported under $v_n=0.87$ represent displacements in petroleum distillate, applied to different cements on the assumption that v_n is the same for all. Values reported under $v_n=0.82$ represent displacements in helium, and the same value of v_n is assumed to apply to specimens prepared by either of the two methods.

There appears to be little theoretical or experimental support for an assumption that $v_n=0.74$, which is to say that the average density of adsorbed water is the same as that of the aqueous solution in fresh paste. The entropy change on adsorption of the strongly adsorbed part [50] is such as to suggest a considerable change of state from that of free liquid. It seems likely that such a change involves a change of density. If there is a change, an increase seems probable, in view of the openness of the structure of liquid water. The value of v_n obtained from helium measurements, 0.82, indicates either that helium is excluded from some spaces accessible to water, or that when water is used as a displacement medium, it is densified by adsorption, or that both factors are involved. Assuming that the difference is due to densification only, it comes out that the specific volume of gel-water ($w_e=3.0\,V_m$; see section 5) is about 0.90 cc/g.

Although the figures for petroleum distillate probably are valid for that fluid, they do not seem to indicate complete penetration of pores. Calculation on that basis shows that the porosity of cement gel to helium is 7 percent greater than the porosity to the distillate.

On the whole, the state of this subject is unsatisfactory. For general purposes it seems that the helium values give the best estimate of v_{hc}.

4. Surface Area of Hydrated Cement and Indicated Size of Primary Particles

Surface Area From Water-Vapor Adsorption

From work reported in 1946 [40] it was deduced that the specific surface area of the solids in mature cement paste is equivalent to that of a sphere having a diameter of 140 A, which is 430 m²/cc, or about 180 m²/g of dry paste. Subsequent work calls for an upward revision of this figure for surface area.

Determination of surface area of hydrated cement is based on water-vapor adsorption interpreted in terms of the Brunauer-Emmett-Teller theory (BET) [41]. A convenient formula is

$$S_{hc}=3{,}800\,\frac{V_m/c}{m+(w_n/c)}\qquad(21)$$

where S_{hc} is the specific surface area of hydrated cement, m^2/g. The numerical coefficient comprises Avogadro's number, the molecular weight of water, and the area covered by a single adsorbed water molecule. Powers and Brownyard [42] used a lower value, 3,570, based on a molecular area of 10.6 A^2/molecule. Recently Brunauer, Kantro, and Copeland [43] concluded that for adsorption of water on tobermorite gel the best value is 11.4. The value 3,800 corresponds to that figure.

Discussion of Eq (21)

BET Surface Factor, V_m

Theoretically V_m is the weight of water required to cover the surface of solid material with a layer 1 molecule thick, and w_n is water that is a component of the solid phase. Actually, there is some uncertainty as to the relations between observed values of V_m and w_n and the theoretically correct values. To obtain the theoretically correct value of V_m the process of adsorption should begin with a "bare" surface. The practice of outgassing with heat to assure this initial condition cannot be followed because the solid tends to decompose when heated. It is necessary to depend on an arbitrarily established drying procedure. Nevertheless, the resulting uncertainty is not such as to destroy the practical value of the data, as is shown especially well by study reported by Tomes, Hunt, and Blaine.

Tomes, Hunt, and Blaine [44] investigated the influence of various degrees of drying of test samples on the experimentally determined values of V_m and w_n. Using the dry ice method described by Copeland and Hayes [36] they tested samples of the same material after seven different periods of drying ranging from 2.6 to 12.1 days, the shortest period giving a value of w_n about 25 percent greater than that given by the longest. Within the range of these data, Tomes, Hunt, and Blaine found that

$$(V_m)_1-(V_m)_2=-0.354[(w_n)_1-(w_n)_2]. \tag{22}$$

Or, in terms of ratios,

$$\frac{(V_m)_1}{(V_m)_2}=1-0.354\,\frac{(w_n)_2}{(V_m)_2}\left(\frac{(w_n)_1}{(w_n)_2}-1\right)\cdot \tag{23}$$

The graph of these data indicates that experimental data would conform to eqs (22) and (23) even to the ultimate values for the given condition of drying. Thus, if the arbitrary drying procedure is too short to remove all the evaporable water, the difference between the observed value of V_m and the correct value is proportional to the difference between the observed nonevaporable water content and the correct one.

Even if the ultimate values of V_m and w_n for a given procedure of drying are obtained, it may be that the humidity maintained in the desiccator is too high to produce a bare surface at the temperature of the experiment. However, inasmuch as the drying conditions used for the experiments of eq (22) are probably not very far from the theoretically correct one, it may be expected that a change to the correct drying condition would result in a relationship like eq (22) with a slightly different value for the numerical constant. Thus, there is reason to assume that the value of V_m obtained by the arbitrarily chosen drying procedure is not very much different from the correct value.

The proportionality between V_m and surface area depends on two factors: (a) average area covered by an adsorbed water molecule, and (b) the difference between the observed and the theoretically correct V_m. The first factor depends not only on the size of the water molecule but also on the structure and composition of the surface on which it is adsorbed. The second factor depends on drying conditions, as just discussed. It thus seems clear that V_m must be "calibrated" for a given material and drying condition. The calibration involves establishing a value for molecular area. The value now used, 11.4 A^2, is that which gave the same surface area by water-vapor adsorption as was obtained by nitrogen adsorption on a laboratory preparation of afwillite. The first estimate of the area of the water molecule on this basis gave 11.8 A^2 [45]. This was later revised to 11.4 A^2 [43]. This method of establishing the molecular area is not the most rigorous that might be devised. Moreover, there is no way to assess the accuracy of the result, other than by the degree to which the computed areas contribute to the internal consistency of various related data. On this score, the results now appear very good.

The values of w_n formerly obtained were about 8 percent higher than those obtained now by the Copeland and Hayes method. Present values of V_m are correspondingly different from the old values. The relationship between the values of V_m now obtained and those formerly obtained may be shown as follows: Using eq (23), let subscript $_1$ denote values obtained by the magnesium perchlorate method, and $_2$ those obtained by the dry ice method. For a particular cement (No. 15754) experimental values were $(w_n/V_m)_2=3.23$, and $(w_n)_1/(w_n)_2=1.084$. With these figures, eq (23) gives $(V_m)_1=0.904\,(V_m)_2$, and $(V_m/w_n)_1=0.258$. This value, based on the Tomes, Hunt, and Blaine empirical eq (23), is the same as that reported by Powers and Brownyard [46] from direct experiment, 0.258 ± 0.002. The exactness of agreement may be somewhat fortuitous, since the cements were not exactly alike.

Maturity Factor, m

This factor is the weight fraction of cement that has become hydrated, i.e.,

$$m=c_h/c \tag{24}$$

where c is the original weight of cement and c_h is the weight of that part which has become hydrated.

(This is *not* the weight of the hydrated cement.) For most cements, apparently all but ASTM Type IV, the following relationships may be used for any intermediate stage of hydration after the first few hours;

$$c_h/c = w_n/w_n^\circ = V_m/V_m^\circ = \Delta H/\Delta H^\circ.$$

(The degree mark indicates that the quantity is for completely hydrated cement.) When the above equalities exist it follows that $\Delta H/w_n$ and V_m/w_n remain practically constant throughout the period of hydration at values characteristic of the cement. This means also that the specific surface area of the hydrated cement remains practically constant at a value given by the following equation:

$$S_{hc} = 3800\left[\frac{w_n^\circ}{c+w_n^\circ}\right]\frac{V_m}{w_n}. \qquad (25)$$

Correction for Calcium Hydroxide

To obtain the surface area of the colloidal part of cement gel (see glossary) it is necessary to make a correction for calcium hydroxide, which has negligible surface area.[3] Eq (26) may be used.

$$S_{\text{col}} = \left[1 + \frac{(CH)}{w_n} \cdot \frac{w_n}{c+w_n}\right] S_{hc}. \qquad (26)$$

(CH) is the weight of calcium hydroxide, and S_{col} denotes surface area of the colloidal part of cement gel, cm²/g dry weight. (CH) may be determined by X-ray analysis, as described by Copeland and Bragg [47].

Experimental Results

Mature Pastes

Data obtained from four different cements are given in table 4, and the results of applying eqs (25) and (26) are given in the first four lines of table 5. In general, the results are the same as those reported previously [48]: The specific surface of cement gel is not affected very much by differences in chemical composition of cement.

The last two lines of table 5 contain data derived from the data of Brunauer, Kantro, and Copeland on the hydration products of C_3S and C_2S [43]. The values of w_n°/c, $(CH)/w_n$, and V_m/w_n were calculated from the data in their table 3, and from the assumption that in colloidal tobermorite the ratio of CaO to SiO_2 is exactly 3/2. The values for S_{hc} are experimental. From a comparison of these data with those in the upper part of the table it appears that the specific surface of the colloidal part of cement gel is from 10 to 20 percent lower than that of pure colloidal tobermorite. Brunauer, Kantro, and Copeland suggested that the sheets and ribbons of colloidal tobermorite may be two or three unit cells thick. The calculated specific surface of a sheet two cells thick is 377 m²/g, and for a thickness of three cells, 252 m²/g. On this basis the colloids in cement gel correspond to a three-cell thickness.

TABLE 4. *Data used for computing surface area of hydrated cement and cement gel*

Reference No.	w/c	Age, days	Number of values averaged	w_n/c	$\frac{V_m}{w_n}$
Clinker 15367; Cement 15754; $(CH)/w_n=1.18$; $w_n^\circ/c=.227$					
B-8-3	0. 40–. 70	81–541	10	0. 2147	0. 304
B-15	. 35	511	1	. 1900	. 317
B-20-1	. 45–. 65	80–543	70	. 2196	. 312
290	. 23	11 yr	1	. 1570	. 287
Weighted average					. 311
Clinker 15623; Cement 15756; $(CH)/w_n=1.36$; $w_n^\circ/c=0.174$					
B-8-3	0. 50–. 65	98–224	8	0. 1593	0. 347
B-15	. 35	513	1	. 1457	. 394
B-20-1	. 55	600	6	. 1693	. 349
290	. 23	11 yr	1	. 1328	. 378
Weighted average					. 355
Clinker 15670; Cement 15763; $(CH)/w_n=0.858$; $w_n^\circ/c=0.170$					
B-8-3	0. 45–0. 65	315–394	4	0. 1525	0. 409
B-15	. 35	505	1	. 1337	. 452
B-20-1	. 55	600	6	. 1506	. 407
290	. 22	11 yr	1	. 1210	. 424
Weighted average					. 413
Clinker 15498; Cement 15758; $(CH)/w_n=1.25$; $w_n^\circ/c=0.210$					
B-8-3	0. 50–. 65	259–300	4	0. 2115	0. 276
B-15	. 35	513	1	. 1870	. 335
B-20-1	. 55	654	6	. 2102	. 294
290	. 23	11 yr	1	. 1711	. 286
Weighted average					. 292

Now that more is known about the morphology of gel particles, it is perhaps pointless to express size of particles in terms of spheres. Nevertheless, for comparison with the earlier figures, it may be noted that a specific surface of 210 m²/g, or about 510 m²/cc corresponds to that of a sphere having a diameter of $6/(5.1\times10^6) = 118$ A, the

TABLE 5. *Calculated surface areas for cement gels, and for the colloidal part of cement gels*

S_{hc}=surface area of hydrated cement, *m²/g*

Reference No.	Computed composition, %				$\frac{w_n^\circ}{c}$	$\frac{V_m}{w_n}$	$\frac{(CH)}{w_n}$	S_{hc}, m²/g	S_{col}, m²/g
	C_3S	C_2S	C_3A	C_4AF					
15754	45. 0	25. 8	13. 3	6. 7	0. 227	0. 311	1. 18	219	267
15756	48. 5	27. 9	4. 6	12. 9	. 174	. 355	1. 36	200	240
15763	28. 3	57. 5	2. 2	6. 0	. 170	. 413	0. 858	227	255
15758	60. 6	11. 6	10. 3	7. 8	. 210	. 292	1. 25	193	235
Average								210	249
Bulletin 86	100				. 200	. 277	2. 439	210	296
Bulletin 86		100			. 160	. 458	1. 344	279	296

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[3] Possibly there are other noncolloidal components, but if so, we cannot measure them at present.

"specific surface diameter". This figure is to be compared with 140 A given by Powers and Brownyard. The same kind of calculation for the colloidal part only gives a specific-surface diameter of 98 A. The figure for cement 15754, the cement from which a great deal of reported data were obtained, is 92 A.

Intermediate Stages of Hydration

As already indicated, to the degree that c_h/c, the maturity factor $m=w_n/w_n^\circ$, and to the degree that V_m/w_n remains constant during hydration of a given cement, S_{hc} is the same at all stages of hydration (eq (25)). The degree of constancy of V_m/w_n has been reported [49]. That early report has been verified by later work, except with respect to Type IV compositions for which the ratio of V_m/w_n changes appreciably during the course of hydration. However, even for those compositions, all the ratios fall within 10 percent of the average. Thus, the specific surface of the hydration products is practically constant so far as this factor is concerned. The validity of the equation $m=w_n/w_n^\circ$ is discussed in other terms in another paper of the Symposium [50]. Such variations as there are in the specific surface values of the successive increments of hydration products are probably insignificant in connection with most considerations involving the internal surface area of cement paste.

Effect of Curing Temperature

Ludwig and Pence [51] reported specific surface as measured by water vapor for pastes cured at elevated temperatures. For a Type I cement cured 7 days, the results shown in table 6 were obtained.

TABLE 6. *Effect of curing temperature on surface area of hydrated cement*

(Ludwig and Pence, 1956)

Pressure	Temperature		$(w_n/c)_8$	Surface area, m²/g of dry paste
	°C	°F		
1 atm	27	80	0.142	103
1 atm	66	150	.162	123
300 psi	93	200	.152	75
300 psi	127	260	.139	30
300 psi	160	320	.139	9

Does Water Vapor Adsorption Give Real Surface Area?

From one point of view, the question is not very important, for that part of the evaporable water that is called adsorbed has certain important physical effects on the system as it enters or leaves whether it occupies space in layered crystals or between them. From a less pragmatic view, the question is important, for a considerable edifice of reasoning about this material can rest on the accepted answer.

There are reasons to question the reality of surface area as it has been measured by water vapor adsorption. For example, Kalousek wrote as follows: "The very large 'areas' of cement pastes obtained by water-vapor adsorption are not true areas. Water apparently enters the lattice of some of the hydrous calcium silicates, perhaps as it does in zeolites or certain clays . . . . The areas computed from total amounts [of water uptake] are, therefore, fictitious." [52] On the other hand, McConnell [53], Miss Moore [54] and probably others, while accepting the fact of interlayer penetration in certain types of crystals, seem to question the assumption that cement gel presents a like situation. Also, it has been suggested that gel water may be water of crystallization (e.g., see H. zur Strassen [55]) and thus is naturally present in fixed ratio to the amount of hydrated cement. There is a great deal of experimental data of diverse kinds bearing on these questions, and it is difficult to assess their meaning. One may observe that evaporable water does occupy space in cement gel, and that such space must have a boundary, but it is possible that the boundary indicated by evaporable water does not coincide with the boundaries of the colloidal crystals. However, there appears to be no compelling need to postulate that this possibility is the actual case. The value for mean distance between particle surfaces obtained from the assumption that lattice penetration does not occur is so small, in relation to the reach of interparticle attraction, that effects that might be attributed to lattice penetration are easily accounted for without postulating such penetration. There is a considerable amount of experimental evidence that lattice penetration does not occur, as will be seen below.

The suggestion that gel water might be hydrate water is not easy to reconcile with the results of permeability tests discussed below and in section 10.

Particle Size From Permeability to Water

Powers, Mann, and Copeland [56] studied the flow of water through specimens of saturated paste in terms of an equation based on the Stokes-Navier law, and obtained a figure for the size of the primary particles (exclusive of calcium hydroxide) in terms of a sphericity factor ϕ and a "volume" diameter, δ. The result was

$$\phi^{1/4}\delta=201 \text{ A}.$$

δ is the diameter of a sphere having the same volume as an average particle in the specimen, and ϕ is defined as the ratio of the diameter, d, of a sphere having the same specific surface as a typical particle in the specimen to the diameter δ of a sphere having the same volume as the typical particle. That is, $d=\phi\delta$. The measured specific surface of the hydrated cement, by water vapor adsorption, gave $d=95$ A after correction for volume of calcium hydroxide. Combining these figures gave the value for sphericity factor

$\phi=0.37$ and $\delta=258$ A. In section 10 a discussion culminating in a revision of these figures is given. The revised data give $\phi=0.41$ and $\delta=233$.

The volume per particle indicated by the value of δ is 9.0×10^6 or 6.6×10^6 A^3, for the first and revised data respectively. If the material were tobermorite gel only, for which the molecular volume is approximately 195 A^3, the average number of molecules per particle would be 49,000, or from the revised datum, 34,000.

To illustrate the significance of the value found for sphericity factor, let us consider a hypothetical gel in which the average volume per particle corresponds to $\delta=233$ A, and assume that the particles are thin sheets such as are found in the hydration product of C_3S. If the width is a, the length b, and the thickness c, then, approximately,

$$\text{specific surface}=\frac{2ab}{abc}=\frac{2}{c},$$

as was pointed out by Brunauer, Kantro, and Copeland [43]. If the sheets are 3 cells thick, c is about 30×10^{-8} cm, or if 4 cells thick, c is about 40×10^{-8} cm, and we obtain specific surface=667 m^2/g, or 500 m^2/cc. The corresponding specific-surface diameters are 90 and 120 A. The sphericity factor for the hypothetical sheet is $\phi=90/233=0.39$, for the 3-cell thickness, and $\phi=120/233=0.52$ for the 4-cell thickness. The value $\phi=0.41$, indicated by permeability test and water vapor adsorption, thus could indicate that the hydration products consist principally of thin bodies containing, on the average, about 40,000 molecules and being about 3 molecules thick.

Perhaps the most significant aspect of the results from permeability studies is the evidence of compatibility between the deductions about particle size from two independent methods. Resistance to flow through a saturated specimen of paste seems to be developed by the same particles which, when dry, adsorb water vapor. As shown in section 10, the permeability data seem extraordinarily amenable to analysis, and the necessary assumptions made in the analysis do not seem to offer enough leeway to invalidate the figures for particle volume. The indicated particle thickness and number of molecules per particle seem too large to support a conclusion that lattice penetration occurs.

Specific Surface by X-ray Scattering

According to Copeland [57] a collimated beam of monochromatic X-rays passing through a granular sample is refracted by crystal lattice planes according to the Bragg law, but if the particles composing the sample are of colloidal dimensions, there is also a scattering by refraction at the surfaces of the particles that does not depend on particle shape or crystallinity. This effect is confined to angles less than about 5° from the direction of the primary beam, and it is therefore referred to as low angle scattering. The scattering due to particle surfaces varies in intensity as a function of scatter-angle as shown in eq (27).

$$((4\pi/\lambda)\sin\theta)=\text{constant}/I. \tag{27}$$

I is the intensity, θ is the angle of scatter, and λ is the wavelength of the beam. The specific surface of the particles composing the sample is given by the following relationship:

$$S_{hc}=\epsilon v_{hc}h^4 I\int h^2 I dh. \tag{28}$$

The left-hand side of eq (27) is represented by h. Copeland applied this method to a sample of the material represented by the first line in table 5. The result was 197 m^2/g. This is to be compared with 219, the figure obtained by water vapor adsorption. This agreement indicates that water vapor gives a real measure, and a fairly accurate one, of surface area. However, there are not enough X-ray data to make this evidence conclusive.

Surface Area by Nitrogen Adsorption

Brunauer, Kantro, and Weise [58] caused C_2S and water to react in a ball mill and found the specific surface area of the product by nitrogen adsorption to be the same as that by water adsorption, provided that the molecular areas of the adsorbates were taken at 16.2 and 11.4 A^2 respectively. The specific surface was about 220 m^2/g. Also, a laboratory preparation of afwillite having a specific surface of about 15 m^2/g showed the same surface area by nitrogen as by water adsorption [45]. But when C_2S and water react in the form of paste, the specific surface area of the product indicated by nitrogen was found to be only 21 percent of that indicated by water vapor adsorption. Surface area indicated by nitrogen adsorption for the colloidal hydration products of C_3S was only about 50 percent of that indicated by water adsorption. In various other experiments made in this laboratory on hydrated portland cement, the surface areas indicated by nitrogen were substantially smaller than those indicated by water vapor adsorption. The same kind of results were reported by Blaine and Valis [59] and by Tomes, Hunt, and Blaine [44]. For example, in the latter report, for neat cement paste, w/c=0.5, cured 1 week, the nitrogen surface area was 22 percent of the water vapor surface area.

Emmett and DeWitt [60] reported that the indicated surface area of anhydrous cement is about 10 m^2/g by nitrogen adsorption, a value much greater than that found by conventional methods. The difference is probably due to the molecular roughness of the surface and possibly due to a very small amount of gel produced by reaction with moisture from the air. Blaine and Valis found the surface area of neat cement, w/c=0.25, to be 10 m^2/g after 1 day of hydration and a little less after 6 months of hydration. In pastes of higher water-cement ratio, the nitrogen specific surface area seems to increase with the progress of hydration up to a certain point, and then ceases to increase. Hunt [61] has observed that, "If one plots water-vapor surface of an initially dried paste against its non-evaporable water content, a straight line is obtained, and the conclusion has been drawn that the gel particles produced at all stages of hydration are the same size. If one makes a similar plot of nitrogen surface areas, using a paste of high water-cement ratio, a curve is obtained which gets steeper with age. It is as if the structural domains measured by nitrogen are getting smaller as hydration proceeds."

All things considered (and there is much more to be considered than is presented here), it is difficult to say what feature of paste structure controls the uptake of nitrogen by a sample. It is clear, however, that the features that govern the uptake of nitrogen vapor are not those that govern the uptake of water vapor.

5. Minimum Porosity of Hydrated Cement Paste, and Specific Volume of Cement Gel

Minimum Porosity

If the cement content of a paste is below a certain limit, and if the paste is kept saturated with water and at normal temperature, all the cement will eventually become hydrated. But, if the cement content is above that limit, the excess will remain unhydrated, apparently for an unlimited period. When the cement content is at the limit for complete hydration, the porosity of a completely hydrated specimen is at a minimum. At any higher cement content, the porosity of the paste is lower only because of the presence of unhydrated cement; the porosity of the hydrated part remains the same.

The first estimate of minimum porosity of the hydration products in cement paste was based on adsorption data, and capacity for evaporable water [62]. The minimum capacity for evaporable water was approximately $w_e/(V_m)_8=4$, w_e being the weight of evaporable water, and $(V_m)_8$ the weight required to form a monomolecular layer on the surface of the solid particles, as determined on samples prepared by the magnesium perchlorate method.[4] Another estimate was based on specific volume measurements, and on this basis the minimum evaporable water content was stated as $w_e/(w_n)_8=0.92$, or, $w_e/(V_m)_8=3.6$, where $(w_n)_8$ is the nonevaporable water content as determined by the magnesium perchlorate method. The computed corresponding figures for specimens prepared by the dry ice method are $w_e/w_n=1.08$, and $w_e/V_m=3.6$, and the helium porosity is about 30 percent.

Although these data were obtained mostly from specimens that had been water cured about 6 months, it was not certain that minimum porosity had been reached [63]. Therefore, additional studies were carried out later by Copeland and Hayes [64]. Using the lowest value found in a group of three dense specimens 11 yr old, they gave $w_e/w_n=0.74$, or $w_e/V_m=2.38$ as minimum evaporable water contents, and the corresponding porosity as 26 percent, these data being on the dry ice basis.

In the course of this review, I considered additional data on minimum porosity as indicated by minimum evaporable water content, with the result given in figure 1. The general relationship it represents is developed from

$$w_t/c=w_0/c+0.254mw_n^\circ/c \qquad (29)$$

where $m=w_n/w_n^\circ$. The second term of the right-hand side is the amount of water that a specimen must obtain from an outside source during the course of hydration in order to remain in the saturated state.

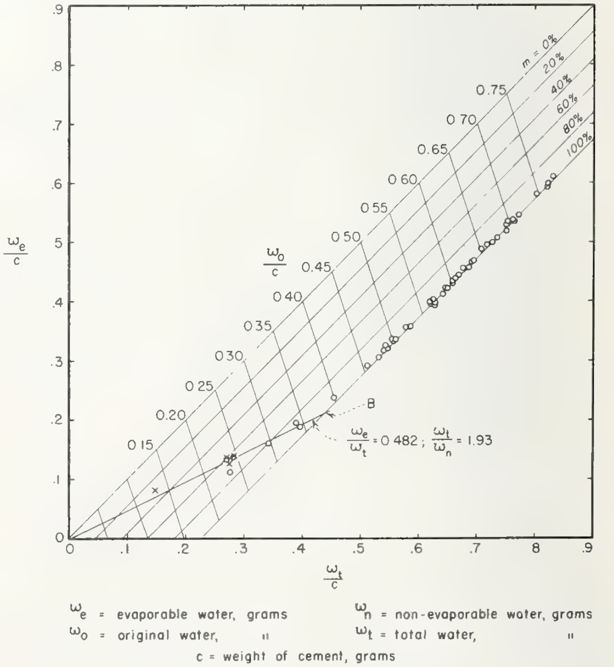

FIGURE 1. *Interrelation of total, evaporable, and original water contents for pastes made with a cement for which* $w_n^\circ/c=0.227$.

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[4] The subscript $_8$ is used as a convenient means of signifying that the datum is from a sample prepared by the magnesium perchlorate method, which method subjects the samples to an ambient vapor pressure of about 8 μ of mercury. Formerly, a subscript $_{1/2}$ was used to indicate sample preparation by the dry ice method, since that method produces an ambient vapor pressure of about ½ μ of mercury, but in this paper absence of subscript has that significance.

The general expressions for amount of evaporable water are:

$$w_e/c=w_t/c-mw_n^{\circ}/c \tag{30}$$

and

$$w_e/c=w_0/c-0.746mw_n^{\circ}/c. \tag{31}$$

For the cement represented in figure 1,

$$w_t/c=w_0/c+0.058m \tag{32}$$

$$w_e/c=w_t/c-0.227m \tag{33}$$

$$w_e/w_t=1-0.227mw_t/c. \tag{34}$$

The plotted points in figure 1 represent fully mature specimens which should conform to eq (33) with $m=1.0$. They do so down to $w_t/c=0.437$ and $w_0/c=0.379$. At all lower values of these two ratios, w_e/w_t remains constant at 0.482, or nearly so, as indicated by the points along line O–B. The corresponding value of w_e/V_m is 3.0; that of w_e/w_n is 0.93.

The ratio $w_e/w_t=0.482$ corresponds to a porosity of 28 percent. This is now considered the best estimate of minimum porosity of dry paste.

When the cement is in excess of that given by $\frac{w_t}{c}=0.437$, the ultimate value of m is less than 1.0. The value is given by $m=2.28\ w_t/c$, or, $m=2.63\ w_0/c$.

Is Stoppage of Hydration Virtual or Real?

Any sample along the line O—B of figure 1 contains both anhydrous cement and chemically free water, i.e., water able to maintain a relative humidity of 100 percent. It is a question, therefore, whether the stoppage of hydration is virtual or real. Czernin [65] carried out two experiments designed to determine whether or not the apparent cessation of hydration in the presence of excess cement is due to the relatively high resistance to diffusion in very dense pastes. If this is the case, the apparent stoppage is not real and is to be explained in terms of relative rates of diffusion. In his first experiment, Czernin used a portland cement paste, "PZ 425", $w/c=0.4$. The paste was water cured 28 days and then ground in a ball mill with added dry cement, reducing w/c to 0.19. After 1 day of grinding, $w_e/w_n=1.06$; after 50 days, $w_e/w_n=0.59$, which seemed to be near a limit. In his second experiment, Czernin used a laboratory-made "alite cement" (90 percent C_3S). The cement was milled with 15 percent water without the initial period of paste hydration used in the first experiment. After 11 days of milling, w_e/w_n reached about 0.61, and seemed to remain constant thereafter up to 40 days, the end of the experiment.

Thus, the two experiments gave nearly the same result. Qualitatively, the result agrees with the data cited above; that is, there is a lower limit to the ratio w_e/w_n. Quantitatively, the results disagree, the ball-mill experiment giving a lower value than any of the values indicated by the other data. The value $w_e/w_n=0.59$ indicated for PZ 425 corresponds to a porosity of about 21 percent.

The meaning of the quantitative difference is not entirely clear. It seems unlikely that the cement represented in figure 1 could differ from PZ 425 enough to account for the difference, since there is no indication that the minimum value of w_e/w_n is influenced much by differences in the composition of cement. Possibly the data mean that a porosity of 21 percent would eventually be reached in pastes, if the curing continued much longer than 11 yr. Another possibility, perhaps more probable, is that the quantity of evaporable water found in the ball-mill experiment is not the same measure of porosity as the quantity found in paste experiments. Dense specimens of paste such as some of those represented in figure 1 are nearly if not quite saturated after continuous water storage for 11 yr. Had they been sealed, without access to curing water, their water content would have been considerably below the saturation point [66, 67]. Perhaps in the ball-mill experiment there was a similar "self-desiccation." If the paste samples had been reduced to the same degree of desiccation before measuring w_e/w_n, the two values of w_e/w_n would have been brought closer together, but neither would have indicated accurately the capacity of the gel for evaporable water. It seems likely that ball-milling would destroy most if not all the structure defined by capillary spaces (see section 6), but it is unlikely that it would destroy the structure of cement gel. Therefore, there is some reason to expect the gel produced in the ball mill to have the same porosity as the gel produced in paste, but there is reason to doubt that evaporable water content is a correct measure of porosity in the ball-mill experiment.

Whether or not hydration in dense pastes actually stops, it is evident that the rate of hydration after several years of curing is so low that it is of no practical interest. If hydration does continue, it does so by an improbable metamorphosis of existing particles, the metamorphosis being such that the interstices among these variously shaped, randomly oriented particles gradually become filled with solid material.

Stoppage of the hydration reactions with both reagents present is not theoretically impossible. The quasi-crystalline hydrates evidently have a naturally restricted growth, possibly due to accumulative misfit of contiguous lattice layers, as suggested by Bernal. After a time when all crystals in a local region have grown as much as they can, further growth requires forming viable nuclei in the presumably supersaturated solution in the gel pores. But in places as small as gel pores, formation of a nucleus of a new crystal would seem a highly improbable event, either from the standpoint of surface energy, or of the size of a unit cell relative to the size of a gel pore. A similar interpretation was advanced recently by Taplin [68].

Specific Volume of Cement Gel

As will be seen in section 6 the massed hydration products in their densest form are called cement gel. The solid matter of the gel together with the characteristic porosity constitutes a solid body having a characteristic specific volume. A general expression for the specific volume of cement paste, on the dry-weight basis, but in the swollen state, is

$$v_p=\frac{v_c+(w_t/c)v_t}{1+w_n/c}. \tag{35}$$

For cement gel, which is composed only of hydrated cement and gel pores, $w_n/c\equiv w_n^\circ/c$, and $w_t/c\equiv w_t^\circ/c$, the last quantity being the total water content of saturated cement gel, including the nonevaporable water. Each quantity is expressed as a ratio to the original amount of cement. Then, eliminating v_t by means of eq (19), we obtain the following expression for the specific volume of cement gel:

$$v_p=v_g=\frac{v_c+0.99\,\frac{w_t^\circ}{c}-0.25\,\frac{w_n^\circ}{c}}{1+\frac{w_n^\circ}{c}}. \tag{36}$$

Complete data for computing the specific volume of cement gel are available for only one cement, PCA lot No. 15754. For this cement, $v_g=0.567$.

The indications are that corresponding values for other cements are similar. Although the values of w_n°/c vary considerably (see table 5) the value of w_t°/c, the total water, is found to be relatively large where the nonevaporable water is relatively small. For the present, we may use for all cements the value 0.567, with due cognizance of the uncertainty.

Ratio of Volume of Cement Gel to Volume of Cement

The volume of cement gel produced by 1 cc of cement may be called the gel-cement ratio, N. By definition,

$$N=(1+w_n^\circ/c)v_g/v_c. \tag{37}$$

For the cement represented in figure 1, $N=2.18$.

Taplin [68] recently advanced a method for obtaining the gel-cement ratio based on the following relationship:

$$N=1+\frac{w_{n^\circ}}{c}\cdot\frac{w_o}{v_c(w_n)_u} \tag{38}$$

where w_{n°/c and $w_o/(w_n)_u$ are for tests at different water-cement ratios. The w_{n°/c represents complete hydration at a water-cement ratio high enough to accomplish this. The w_o and $(w_n)_u$ represent, respectively, the initial amount of water and the ultimate value of w_n for a water-cement ratio low enough to assure an excess of cement. Equation (37) should give a more accurate result than eq (38) because it is based on the total water content of a saturated specimen at the time of analysis rather than on the original water content. If the original water content is used it should be corrected for any decrease during the bleeding period, and for increase due to expansion of the specimen during the curing period.

6. Concepts of Structure of Cement Gel and Cement Paste

Evolution of Models

Powers and Brownyard [69] used drawings suggesting that dense masses of gel particles form in and around the sites of cement grains, and that these masses generally do not fill all the space between the original boundaries of cement grains. Later, Powers and Helmuth [70] presented the same idea in greater detail, representing the gel particles as spheres. Originally, this assumption as to shape was adopted for simplicity and convenience, but later [71] some electron micrographs indicated that the particles actually were spherical, and this was mentioned in the paper referred to. In later publications [72, 73] drawings showing the particles to be platy, or ribbonlike fibers, were used, in harmony with electron micrographs by Grudemo from calcium silicate hydrates [74] and from cement paste [75] (see fig. 2). Such drawings give a meager outline of a concept of structure. One may fill in details on the basis of data on the size and shape of particles, the space required by hydrated cement, and the mode of formation of cement gel. It is necessary to deduce various details that are not directly observable. Such deductions are more or less speculative, and it is to be expected that not all will agree on the dividing line between valid deduction and questionable speculation.

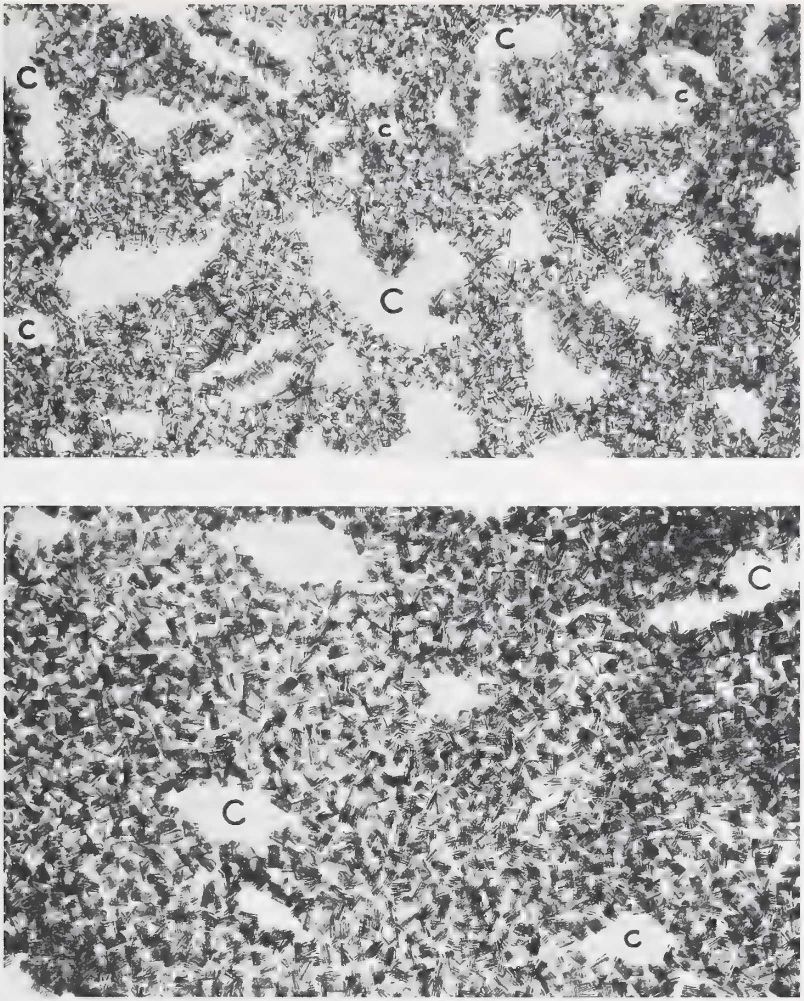

FIGURE 2. *Simplified model of paste structure.*

Masses of randomly oriented groups of black lines represent cement gel. Spaces like those marked C represent capillary cavities. Upper drawing represents mature paste, $w_o/c=0.5$, capillary porosity 20%; lower drawing represents nearly mature paste, $w_o/c=0.3$, capillary porosity 7%.

Space Requirements

As shown in section 5, it is known that cement gel requires about 2.2 cc of space per cc of cement. This means that 1 cc is formed inside the original boundaries of the cement grains, and 1.2 cc is formed outside, in the originally water-filled space. (Taplin's paper [68] indicates that he also made this observation, and developed concepts similar to those described below.)

Mode of Gel Formation [76]

After an initial process peculiar to conditions that can exist only a short time, the main part of the hydration process seems to start at the grain boundaries, and cement gel grows outward and inward simultaneously, each grain residue being continuously encased in gel as long as it exists. Water diffuses inward through the gel pores while the components of hydrated cement, presumably in a state of supersaturated solution, diffuse in the opposite direction to the outer border of the gel layer, where they add on to existing crystals, or start new ones. Approximately 55 percent is transported outward, and 45 percent stays inside.

It is reasoned that since the hydration products in a specimen of paste containing an excess of cement ($w_o/c<0.38$) can eventually produce a gel having a porosity of 28 percent, that same degree of density can be, and is produced locally at various places throughout the paste, even when the cement is not in excess. The part of the gel that is formed by inward growth is produced under the greatest possible concentration of reagents. It seems, therefore, that at least 45 percent of the gel in any specimen has minimum porosity. Also, since every grain of cement in the flocculent, fresh paste (see section 2) is practically in contact at several points on its surface with neighboring grains, the outward-growing gel should reach minimum porosity at these points early in the process. It is not known, of course, whether the minimum porosity reached in the outside material is the same as that of the inside material, but whatever the case may be, it may be assumed that there is a range of pore sizes in the gel as a whole. The smallest size might be of a monomolecular dimension; the largest would seem to be that size just smaller than the smallest in which nucleation is possible. On this basis, it would seem that the overall porosity of any region containing only pores within the size range just described (and consisting of approximately equal portions of the "inside" and "outside" product) is the 28 percent mentioned above. It follows that any region where the porosity exceeds 28 percent is also a region where new crystals could nucleate, or already existing crystals could continue to grow; in other words, it is a region where pores exist that are larger than the largest characteristic of cement gel. During the process of hydration, the components of hydrated cement that are diffusing outward from a grain will be likely to be deposited in the first over-gel-size pore encountered. Thus the "outside gel" tends to achieve characteristic gel porosity as it grows. This idea is expressed in figure 2 by showing the capillary spaces to be orders of magnitude larger than gel pores. However, it is clear that as a given local region approaches minimum porosity, the remaining capillary pores in that region will gradually become indistinguishable from gel pores, and this idea is represented by some areas in the drawing where only slight gaps in the gel appear. One sees the possibility, if not probability, of the gel particles formed by inward growth having a different morphology, and perhaps even a different stoichiometry, from the particles formed by outward growth.

Size of Gel Pores

Powers and Brownyard [77] estimated the width of pores in cement paste from the ratio of pore volume to surface area, i.e., the hydraulic radius. With the data then available, the figure obtained for the hydraulic radius was 10 A. This meant that the average width of pore lay between 20 and 40 A, probably closer to 20 than to 40. From data given in preceding sections we have

$$\text{Hydraulic radius} = \frac{w_e v_e}{38 \times 10^6 V_m}$$

$$= 2.6 \times 10^{-8} v_e \frac{w_e}{V_m} \text{ cm} = 2.6 v_e \frac{w_e}{V_m} \text{ A.} \quad (39)$$

As shown in section 5, the minimum value of w_e/V_m is about 3.0, and therefore the hydraulic radius of the gel is $7.8 v_e$ A. The specific volume of gel water is not known exactly. On the basis of the specific volume of hydrated cement as given by helium displacement, it is 0.9, and this figure gives a hydraulic radius of 7.0 A. The corresponding average distance between solid surfaces in the gel is between 14 and 28 A, 18 A being a reasonable estimate. This distance is about 5 times the diameter of an unbonded oxygen atom, or about 13½ times the diameter of a single-bonded oxygen atom. The unbonded diameter, 3.6 A, is about the same as that of a water molecule.

Size of Capillary Spaces

No systematic attempts to measure the size of capillary spaces have been reported. However, various observations show that they are generally orders of magnitude larger than gel pores. When there are capillary spaces, reflected light is scattered. Such scattering signifies the presence of randomly arrayed structural discontinuities several hundred angstrom units apart. (These are the reasons why mature paste of high quality has a dark, bluish-gray cast, whereas paste of low quality appears much whiter.) Other direct evidence of the relative largeness of capillary spaces will be found in section 10 which deals with permeability to water. When the total porosity of cement paste is increased by reducing the amount of gel and increasing the capillary space, the rate of increase in permeability shows that the capillary spaces are very much larger than gel pores.

Summary Description of Cement Paste

Although the concept illustrated in figure 2 is in several ways oversimplified, it is a useful aid toward understanding the properties and behavior of cement paste and concrete. The main features of paste structure may be summarized as follows: *cement gel* is a rigid substance that occupies about 2.2 times as much space as the cement from which it was derived. Its porosity is about 28 percent, and the average width of its pores is about 18 A, which is about 5 times the diameter of a water molecule. There is evidence that the gel particles are in contact with each other at many points and that some of the points of contact are chemically bonded. The porosity of cement gel is a natural consequence of the growth of irregular particles in random directions from randomly distributed starting points. Cement gel is mostly colloidal matter, but, as defined here, it contains noncolloidal material also, chiefly calcium hydroxide.

Cement gel is one component of cement paste. The other component is the residue of originally water-filled space that has not become filled with gel. These spaces are called *capillaries* or *capillary cavities*. When capillary porosity is relatively high, the capillaries are a continuous interconnected network through the gel, but at normal paste porosities, capillary spaces are interconnected only by gel pores and are accordingly called capillary cavities. The properties of cement gel and the degree to which the gel is "diluted" with capillary spaces, and the effects of water in gel pores and capillaries are factors that determine important characteristics of concrete.

Paste may also contain a residue of anhydrous cement.

Computation of Capillary Porosity of Paste

Since the capillary porosity is a significant factor, fundamental studies of strength, stress-strain-time characteristics, permeability, and durability could be facilitated by dealing with it quantitatively. Convenient means of a computation are indicated in eqs (40) and (41).

$$\epsilon_c=1-\frac{cv_c}{V}\left[1-m+m(1+w_n^\circ/c)\,\frac{v_g}{v_c}\right] \qquad (40)$$

$$\epsilon_c=1-\frac{m\left[(1+w_n^\circ/c)\,\frac{v_g}{v_c}-1\right]+1}{1+\frac{w_0/c}{v_c}}. \qquad (41)$$

Here ϵ_c is the capillary porosity; v_g is the specific volume of cement gel in cc/g of dry gel. (See section 5.)

7. Mechanical Effects of Adsorption and Hydrostatic Tension

This section may be regarded as an extension of section 6, for a concept of physical structure is sterile unless it is combined with some understanding of the interaction of the solids and evaporable water, which is the present subject. Quantitative data are few, but those given by Powers and Brownyard [78], together with more recent unpublished results, provide a basis for discussion.

Adsorbed Water and Capillary-Condensed Water

At temperatures above the freezing point, chemically free water molecules present in cement paste at any humidity below 100 percent would be gaseous and of negligible amount were it not for forces that hold nearly all of them in a condensed state. All surfaces are usually covered with water molecules, and, except at low humidities, capillary cavities contain water. Powers and Brownyard [79] observed that the amount of water held at any relative humidity below about 40–45 percent (25 °C) was proportional to the internal surface area, i.e., the surface area of the gel particles in the specimen, but at humidities higher than 40–45 percent the amount of water taken up by a dry specimen depended on the porosity of the specimen. It was therefore concluded that at humidities below 40 percent the water was held entirely by adsorption forces, and that most of the water taken up at humidities well above that limit is held by capillary condensation.

The theory of nucleation helps us to understand this observation and deduction [80]. Two different theories of the nucleation of vapor bubbles in pure water under negative pressure at room temperature lead to the result that the "fracture strength" of water is about −1200 atm. This is the negative pressure giving a probability of unity for the spontaneous nucleation within about 1 sec of a vapor bubble by thermal fluctuation of the water molecules in the liquid [81]. The theoretical fracture stress based on nucleation occurring within 1 yr is about −1100 atm [82]. Under such stress, water molecules are unable to cohere, and since a meniscus depends upon molecular cohesion, capillary condensation becomes impossible. It happens that the relationship between the pressure in the liquid phase and the corresponding equilibrium vapor pressure gives, as computed by Barkas [83], −1200 atm at a relative humidity of 40 percent, and −1100 at 45 percent. Thus, the observation that water in cement paste at humidities below about 40 percent is not subject to capillary condensation is in agreement with the theoretical deduction that a meniscus cannot exist below such a humidity. Perhaps that agreement may be regarded as strong support to the theory of nucleation as a means of arriving at the cohesive strength of water, although the fact that water in cement paste is not pure injects some uncertainty as to whether the agreement ought, theoretically, to be as close as indicated. Nevertheless, it seems justifiable to assume that part of the water held in a specimen at humidities above 40–45 percent has the ordinary properties of liquid water. The water held at a humidity of 45 percent is somewhat less than enough to make two complete molecular layers over the surfaces of the solid phases, and such a film does not have the properties of liquid water. Its condensed state is due to the forces of adsorption.

In a specimen saturated with water and surrounded with water or a water-saturated atmosphere, there is no hydrostatic tension, and as we have seen, some of the water contained in the pores exhibits the normal properties of water. The first question to be considered is how capillary water is lost from the specimen during drying, particularly the first drying.

The Process of Drying

When a small container made of a hydrophilic material contains both air and water, the boundary between the water and air is a meniscus concave toward the air. Water in a glass capillary, bounded at each end by a meniscus, is a familiar example. When water evaporates from such a capillary, it seems that evaporation occurs from the meniscuses, and, from Kelvin's equation, it is understandable that the tendency of water to evaporate is reduced because of the negative pressure in the water induced by the curved surfaces. On the basis of an analogy between a porous solid and a "bundle" of capillaries, it is sometimes assumed that the drying of a specimen of saturated cement paste involves evaporation from the meniscuses in the capillaries within the paste.

We have already seen that the bundle-of-capillaries concept is hardly compatible with evidence concerning the structure of cement paste. It is safe to say that in all cement pastes some of the capillary spaces are in the form of cavities isolated by cement gel, and in some cement pastes, perhaps most, *all* the cavities are so isolated. (See also section 10.) If we are to assume that, during drying, evaporation occurs only from curved surfaces, none of the water in isolated capillary spaces can evaporate until the humidity drops sufficiently low to cause evaporation from the very small gel pores of the surrounding gel. Indeed, a theory of adsorption-desorption hysteresis is based on the notion that such a situation is analogous to an ink bottle: the inside communicates with the outside only through the neck and therefore the contents of the bottle cannot escape by evaporation until the neck has been emptied.

The amount of water lost from cement pastes at relatively high humidities cannot be accounted for on the basis of the theory just mentioned. Water in capillary spaces surrounded by gel evidently does escape at high humidities even though it is not able to present a liquid surface from which evaporation can occur. A different theory that takes into account some consequences of hydrostatic tension is required to account for the observed facts.

When water evaporates from the outside surface of a body of cement gel enclosing one or more water-filled capillary spaces, hydrostatic tension develops, as is shown by the reduction of water-vapor pressure of the water remaining in the body. The magnitude of the tension is limited by the relative humidity of the surroundings. One consequence of hydrostatic tension is that if the water is initially saturated with air, it immediately becomes supersaturated, the degree of supersaturation being a function of the hydrostatic tension. When the degree of supersaturation is sufficiently high, bubbles can develop in the capillary cavities. The degree of supersaturation and hence the magnitude of hydrostatic tension required to produce bubbles depends on several factors, as discussed below. The discussion follows that of Bernath [81].

Let us consider first the conditions necessary for static equilibrium between a bubble and its surroundings, neglecting the force of gravity. The bubble is surrounded by capillary water, and the capillary water is continuous with the gel water that permeates the surrounding structure. The bubble is assumed to be spherical and to contain n molecules of gas, including molecules of water vapor. Let P_b represent the gas pressure in the bubble, and $4\pi r^3/3$ the volume of the bubble, r being the radius. The following "perfect gas" equation gives the free energy content of the bubble, on the left side in terms of the product of pressure and volume, and on the right side in terms of the kinetic energy of the gas molecules.

$$P_b\left(\frac{4}{3}\pi r^3\right)=n_bkT. \tag{42}$$

T is absolute temperature; k is Boltzman's constant (energy per molecule per degree) and n_b is the number of molecules in the bubble. The pressure in the bubble is also equal to the pressure exerted on the gas by its surroundings, that is

$$P_b=P_C+\frac{2\gamma}{r}. \tag{43}$$

P_C is the hydrostatic pressure in the capillary water and γ is the surface tension. The second term on the right-hand side is the capillary pressure due to the spherical meniscus of the bubble. In the present case,

$$P_C=-t \tag{44}$$

where t is hydrostatic tension. Substituting from eqs (43) and (44) into (42), we obtain eq (45):

$$\left(\frac{2\gamma}{r}-t\right)\left(\frac{4}{3}\pi r^3\right)=n_bkT. \tag{45}$$

This equation shows that at a given temperature the free energy content of a bubble is a function of the radius of the bubble. The function is such that the free energy content of the system increases with an increase of r up to a critical value r^*, and for larger values of r, the free-energy content decreases. From this it follows that if a bubble having a radius smaller than r^* should develop, it would probably disappear (dissolve) immediately, but if the radius quickly becomes equal to r^*, the bubble is just as likely to remain as to disappear. Therefore a bubble is likely to be viable if at one instant it can form with a radius greater than r^*. Such a phenomenon can happen only when the water becomes sufficiently supersaturated with dissolved air. When the water is initially saturated with air, bubbles evidently can form with relatively little hydrostatic tension. This is indicated by the fact that relatively large amounts of evaporable water are lost at high humidities. However, it seems clear that bubbles can form only in those capillary spaces large enough to permit a viable nucleus to form, that is, only in those cavities having a radius greater than r^*.

The necessary size of cavity is that which will accommodate a nucleus having a radius slightly larger than r^*, and able to accommodate also a layer of adsorbed water molecules that cannot become a part of the meniscus of the bubble. The thickness of this layer is estimated to be about 5 A.

The value of r^* can be obtained by differentiating eq (45) with respect to r, with T constant, and with $t=t^*$, where t^* is the value of tension at which nucleation is possible. The derivative is then equated to zero, and the equation is solved for r. The result is

$$r=r^*=\frac{4}{3}\frac{\gamma}{t^*}. \tag{46}$$

On comparing eq (46) with eq. (43), with $P_C=-t^*$, we see that eq (46) is not a statement of static equilibrium. In other words, the nucleation radius, r^*, is not the same as the stable radius for static equilibrium at the hydrostatic tension t^*. The expression for equilibrium is

$$r_s=\frac{2\gamma}{t^*+P_b}\approx\frac{2\gamma}{t^*}\text{ when }P_b<<t^*. \tag{47}$$

The value of r_s, the size that would be stable at tension t^*, is not of special interest in the present connection. It only indicates that if t^* is established and kept strictly constant, the bubble would nucleate and the radius would increase about 50 percent to establish equilibrium. Except when r^* is so small that thermal fluctuations might disturb equilibrium, static equilibrium is quite possible. However, the equilibrium is rather unstable in any case, since even the slightest increase over t^* would permit the bubble to expand to the limit fixed by the dimensions of the cavity.

The pores in cement paste range in size from molecular dimensions upwards to perhaps 0.1 μ, the upper limit actually being unknown. Table 7 gives the calculated nucleation radius for different levels of hydrostatic tension and the corresponding values of required cavity size, assuming the cavities to be spherical. If, for example, drying has occurred at a relative humidity of 96 percent, all cavities having radii greater than about 175 A would be able to accommodate the nuclei that could form at that humidity, and all the cavities smaller than that size would remain full of water. When the humidity has dropped to the 50 percent level, all cavities having radii greater than about 15 A should contain bubbles. However, as noted in the table, at humidities below about 45 percent, bubbles cannot exist because the hydrostatic tension exceeds the fracture strength of water, and therefore phenomena arising from molecular cohesion of water disappear. The formation of a meniscus is one such phenomenon.

As shown above, at any given humidity all the capillary cavities below a certain size (table 7) will remain full whereas each of the larger ones will contain a bubble. Nevertheless the hydrostatic tension must be the same in the cavities containing bubbles as in those not containing bubbles. Therefore, beginning with the saturated state, the hydrostatic tension that develops as the specimen is dried to a lower humidity is, after a state of equilibrium has become established, the same throughout the capillary space as if all the capillary space had remained filled with water while the tension developed. Thus shrinkage caused by drying at humidities above about 45 percent is a hydrostatic compression, and the amount of hydrostatic compression depends upon the elastic and inelastic time-dependent deformation characteristics of the paste.

TABLE 7. *Computed inscribed diameters of capillary cavities able to contain spherical bubbles at given humidities (eq (46))*

Relative humidity	Hydrostatic tension	Nucleation radius r^*	Required radius of spherical cavity r^*+5
Percent	*atm*	*A*	*A*
98	28	346	351
96	57	170	175
92	116	84	89
85	226	43	48
70	495	20	25
50	963	10	15
45	1,100	([a])	
40	1,200	([a])	

[a] Bubbles cannot exist at tensions above the fracture strength of water, which is apparently between −1,100 and −1,200 atm.

Only a few data on the shrinkage of mature cement paste samples dried under suitable conditions are now available, but there are some, obtained about 20 yrs ago, from specimens dried in CO_2-free air at four different humidities. An example of the results obtained is shown in figure 3. The changes in volume for drying at humidities of 75, 45, 18, and 1 percent are plotted against the computed tensions for those humidities. These data,

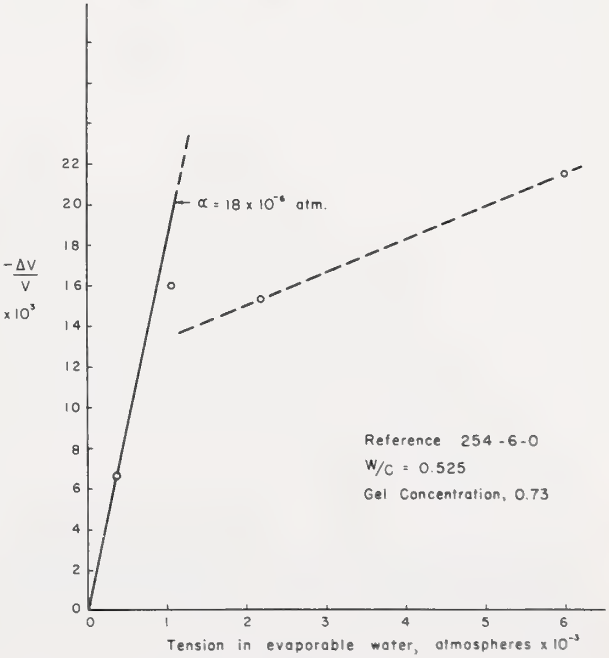

FIGURE 3. *Shrinkage vs. tension.*

considered together with data for various other specimens, indicate that a shrinkage-vs.-stress curve for tensions up to about 1,000 atm resembles one for mechanical loading. Shrinkage is approximately proportional to stress, departure from linearity being greater the higher the capillary porosity of the paste. The slope of a line from the origin to a point representing shrinkage at a given tension gives the coefficient of compressibility [5] for the indicated sustained, isotropic tension. The value indicated in figure 3 is 18 millionths per atm, and that figure appears to apply to all tensions up to about 900 atm, but some curvature would probably be seen if more points were available, since some of the compression is inelastic, and such deformation is not usually exactly proportional to stress. A compressibility of 18 millionths per atm corresponds to a Young's Modulus of about 1.5×10^6 psi or 100 kg/cm^2, which is reasonable for the ratio of stress to strain for such a paste under sustained load.

Other data show that when shrinkage stress is released by soaking the specimen in water, the amount of expansion per unit change of stress agrees approximately with the modulus of elasticity of the paste as determined from the resonance-frequency of vibration of a test prism. This is one aspect of the stabilization of paste structure discussed in section 8.

From the above discussion of the fracture strength of water, one might expect some sort of discontinuity in the stress-strain diagram at a tension of about 1,100 atm. A discontinuity does seem to be indicated by these data (fig. 3) but the points are too few to establish the locus exactly. It is not clear whether the transition should be abrupt or gradual, but an abrupt transition seems probable because when the stress in the water reaches the breaking point, which, for 1 yr of sustained stress would be about $-1{,}100$ atm, stress due to surface tension in the capillary cavities should disappear. This would reduce the effective area from unity to $1-A_c$, where A_c is the cross-sectional area of capillary spaces that contained bubbles, per unit overall area. If we assume that the break occurred at $-1{,}150$ atm, and that expansion is proportional to the reduction of effective area, the indicated value of A_c is about 20 percent, which is not far from the actual capillary porosity of the specimen. After the transition point, further increases in tension are accompanied by progressive emptying of the gel pores and decreasing of the area factor. Thus, for the specimen represented by figure 3, one might suppose that the compressibility coefficient remains about the same while tension increases, but the area factor falls off in such a way as to give the observed diagram.

From this approach, it would seem that as the area factor approaches zero, effective tension approaches zero, and the specimen should expand. This is not the case, however; at the point where all the evaporable water has become lost, and the area factor has become zero, shrinkage is at the maximum possible for the temperature of the experiment. To understand this result, gel structure must be taken into account.

Areas of Obstructed Adsorption

The observed result seems to be due to obstructions that prevent adsorbed water from spreading evenly over the surfaces of the particles. The obstructions are probably in those areas where contiguous particles are bonded to each other, the distance of separation being zero, and in areas (presumably adjacent to those spots) where the surfaces are separated, but not separated enough to accommodate as many water molecules per unit area of surface as could be held in areas of unobstructed adsorption. The evidence of the existence of *areas of obstructed adsorption*, is the same as that indicating the existence of interparticle bonds, and the nature of shrinking and swelling phenomena itself.

Those water molecules that are excluded from areas of obstructed adsorption maintain a pressure—a film pressure—that tends to separate the obstructing surfaces. This film pressure thus causes a slight dilation, or swelling. The amount of swelling produced by film pressure is limited by tensile force corresponding to stress in the bonds that hold the gel particles together. Swelling pressure, and tensile stress in the bonds, is greatest when the specimen is saturated and thus when tension in the evaporable water is nil. When tension in evaporable water appears, swelling pressure is correspondingly diminished and tensile stress and strain in the bonds also. The reduction of swelling pressure is effective in areas of obstructed adsorption only, but, as already shown, when hydrostatic tension is less than the fracture strength of water, hydrostatic tension is effective over the whole area of the paste, and the specimen becomes compressed more than can be accounted for by reduction of swelling pressure only. However, at tensions above the fracture strength of water, further increase of tension serves only to reduce swelling pressure in areas of obstructed adsorption. The effective areas of obstructed adsorption must become smaller as the water content is reduced, reaching zero when all the water has become evaporated. Thus, shrinkage in the high-tension range is primarily caused by cohesive forces between the solid bodies of which the gel is composed.

During the last stages of removal of evaporable water, there is enough increase in interfacial energy at the solid surfaces to cause an increase in specific gravity of the particles and corresponding shrinkage, but this is now believed to be a minor contribution to the total change shown in figure 3.

Effect of External Pressure

Although no direct experimental confirmation can be cited, the foregoing discussion of internal forces leads directly to conclusions pertaining to the effects of applying pressure externally. If a specimen of hardened paste at equilibrium with the ambient humidity is subjected to an *isotropic* pressure applied to the external surface, the compressive force on the water films in areas of obstructed adsorption maintained by tensile stress in the solid bonds is thereby augmented. Some of the water is displaced immediately from the areas of obstructed adsorption, and since the water lost from the loaded areas must be gained by the rest of the area, the internal humidity rises. A rise of internal humidity produces an increase of swelling pressure, opposing the external pressure and, in effect, the specimen swells. To restore equilibrium with the ambient humidity, some water eventually evaporates, and the swelling pressure falls to its original level, with a further compression (shrinkage) of the specimen.

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[5] As defined here, compressibility is $\frac{\Delta V}{\Delta P}\cdot\frac{1}{V_0}$, where V_0 is the volume in the saturated state.

If the specimen had been subjected to isotropic tension, rather than isotropic compression, the effect would have been as follows: the compressive force on the water films maintained by the cohesive bonds of the gel would have become diminished, and there would have been a concomitant widening of the spaces in the areas of obstructed adsorption, thus creating a deficiency of water molecules in those areas. Molecules from the unobstructed areas would diffuse into the areas of obstructed adsorption, but in so doing, the internal humidity is caused to decrease, the film tension to increase correspondingly and the specimen is caused to shrink. However, to restore equilibrium with the ambient humidity, water molecules from the outside would be received until the original humidity was regained. During the time required for this process, the specimen gradually dilates (swells) under the sustained external tension, finally annulling the shrinkage induced by the application of the external isotropic force.

If external pressure is applied uniaxially, as for example by loading the ends of a cylinder, a combination of effects of isotropic compression and isotropic dilation should be present. Spaces between surfaces oriented principally normal to the axis of the cylinder would be reduced, and those oriented principally parallel to the axis would be increased. The effect is a temporary swelling counter to the direction of compression, and shrinking counter to the lateral extension. Establishing a new state of equilibrium requires transfer of water from the compressed areas to the extended areas, but there may be no appreciable change in an average internal humidity, and hence no change in weight of the specimen.

The foregoing discussion accounts, at least in part, for the time-dependent part of elastic response to an external force which was shown especially well by recent data published by Glucklich [84]. In addition to time-dependent elastic response, there is also a time-dependent inelastic response, apparently related to, if not a direct manifestation of, the instability of cement paste discussed in section 8.

Freezing of Evaporable Water

Following the pioneer work of von Gronow [85], Powers and Brownyard [86] studied the freezing of water in cement paste by means of dilatometry. They showed that at any subfreezing temperature some of the evaporated water remains unfrozen, and for temperatures below −6 °C the amount unfrozen is proportional to the surface area of the gel. At temperatures between 0 and −6°, the amount remaining unfrozen at a given temperature is not proportional to the surface area. Recently, Helmuth [87] found that the departure from proportionality is due to the presence of solutes in the evaporable water, principally sodium hydroxide and potassium hydroxide. In general, the findings have been as would be expected from the characteristics of the sorption isotherms.

Verbeck and Klieger [88] reported the amounts of ice formed in concrete, as measured by the change in heat capacity during cooling. Typical results are given in table 8. The last column of table 8 shows the amount of expansion of water that must be accommodated by space in the concrete during freezing, expressed as a percentage of the total volumn of concrete. It is clear that concrete normally contains more than enough voids to accommodate the expansion of water caused by freezing, and therefore the destructive effect of frost is not due to lack of space in the concrete for expansion of water. Frost action is the subject of another paper of this Symposium [89], and will not be pursued further here.

TABLE 8. *Amount of water frozen at −20 °C (−4° F) in concrete cured 7 days before freezing*

(Verbeck and Klieger, 1958)

w/c	Cement content lbs/yd^3	Amount of ice at −20 °C(−4 °F), percent of concrete vol.	Percent frozen at −7 °C(20 °F)	Water expansion per cent of concrete vol.
0.41	660	3.8	93	0.35
.49	520	4.9	70	.45
.72	380	8.1	57	.75

8. Instability of Paste Structure

Spontaneous Reduction of Specific Surface Area

Because of its high surface area, cement gel is often referred to as a metastable substance on the grounds that if large gel particles were to grow at the expense of small ones, a substantial reduction in specific surface area and in specific free energy content of the gel would take place. Evidence of such a change would be a reduction in the ratio V_m/w_n, which ratio is proportional to the reduction in specific surface area. Over the years during which measurements of V_m and w_n have been carried on, no reduction in the ratio has occurred for any specimen kept continuously moist. This indication of stability may be accounted for in part by the morphology of hydrated cement. If cement gel is made up of thin sheets or ribbonlike fibers, a substantial reduction of surface area and surface energy would require more than mere growth, for if a large sheet became longer and wider while a smaller one changed dimensions oppositely, the resulting reduction in surface energy would be very small. Any substantial reduction in surface area and free energy would require a more profound metamorphosis, particularly a strong tendency toward isometry along with increase in size.

Under conditions other than continuous moist storage, the story is quite different. In an autoclave at temperatures upwards of 100 °C, the kind of metamorphosis mentioned above occurs readily, accompanied by some change in stoichiometry. Powers and Brownyard [90] found the specific surface area of autoclaved hydrated cement to be only 5 percent of that of hydrated cement cured in the ordinary way. Ludwig and Pence [51] obtained a similar result. See table 6 of section 4.

Not so widely known is the discovery by Tomes, Hunt, and Blaine [44] that the very process of determining the surface area of cement gel by water-vapor adsorption causes a reduction of specific surface. After drying samples from the saturated state to a relative humidity of about 0.00002, they carried out eight cycles of adsorption and desorption, the adsorption being in four steps as required by the BET procedure, and the desorption in one step. The range of humidities was from 0.00002 to 0.33. Their data, obtained on granulated samples, are given in table 9.

TABLE 9. *Reduction of specific surface area, caused by cycles of desorption and adsorption*

(Tomes, Hunt, and Blaine, 1957)

Cycle	Specific Surface m²/g of dry sample	Relative surface area
1st adsorption	89. 9	100
2d adsorption	75. 8	84
3d adsorption	66. 5	74
4th adsorption	63. 2	70
5th adsorption	58. 8	65
6th adsorption	57. 5	64
7th adsorption	56. 0	67
8th adsorption	56. 3	63

Although the change in surface area produced in this way is much less than that produced in the autoclave, it is substantial and significant with regard to various aspects of concrete technology, as well as to laboratory studies. From the trend of the plotted data, it appears that, if the reduction in specific surface occurs during desorption, as seems likely, the original surface area was reduced at least 20 percent before the first adsorption, and thus, by the sixth adsorption only half the original surface remained.

Other experiments were made by the same authors in which the samples were completely saturated between successive BET determinations. The second adsorption gave 97 percent of the area indicated on the first adsorption and the third adsorption gave 89 percent. These figures are to be compared with 84 percent and 74 percent in table 9. Thus, allowing the material to swell as much as possible between surface area determinations seems to undo some of the effect of desorption.

In a recent paper, Hunt, Tomes, and Blaine [91] report additional observations on spontaneous reductions of surface area occurring while samples are in storage in sealed containers. Completely dry samples seemed to be stable, but those containing small amounts of evaporable water, left in the samples deliberately, were unstable. Some of the data are given in table 10. The maximum rate of spontaneous change was found in samples that produced a humidity of about 50 percent in the sealed containers. (The humidity was determined by direct measurement.) The samples that produced humidities below 1 percent and above about 80 percent seemed to be stable.

TABLE 10. *Changes in specific surface area occurring in sealed specimens as a function of amount of residual evaporable water*

(Hunt, Tomes, and Blaine, 1960)
w_e=weight of evaporable water in the sample.
c_i=weight of ignited cement.

$\frac{w_e}{c_i}$	V_m/w_n after storage period indicated		Relative surface area after storage period indicated	
	1 month	21 months	1 month	21 months
0. 006	0. 300	0. 295 [a]	100	98 [a]
. 02	. 295	. 280	98	93
. 06	. 265	. 243	88	81
. 10	. 262	. 230	87	77
. 17	. 282	. 277	94	92
. 20	. 300	. 300 [a]	100	100 [a]

[a] Estimated by extrapolation.

The nature and cause of a reduction in specific surface under the conditions described above remains a matter for speculation. Collapse of a layered structure naturally suggests itself, and Tomes, Hunt, and Blaine offered, tentatively, such an explanation. Other data that appear to be incompatible with such an explanation have already been presented (section 4) and more may now be introduced. Tomes, Hunt, and Blaine found that wetting and drying not only reduced the surface area as measured by water but also reduced the values found by nitrogen. For the specimens that were subjected only to humidity fluctuations between 0 and 33 percent, the nitrogen area was reduced by about the same percentage as the water area. For the specimens represented in table 10, the nitrogen areas were reduced *much more* than the water areas. If water vapor actually penetrated the primary particles, primary with respect to nitrogen adsorption, a reduction of such penetration by water should reduce the indicated water area but not the nitrogen area.

Perhaps the most plausible explanation is that during desorption, gel particles are brought closer together than they have ever been before, and new points of contact are produced under considerable pressure. (See section 7.) If this should create stable chemical bonds between the particles, the irreversibility would be accounted for. If the evidence is construed to indicate such new bond formation, it indicates also that the bonds have various degrees of strength. As shown in table 9 not all possibilities for forming new bonds are exhausted at one time, so that repeated cycles are required to establish stability under a given set of conditions. Also, considering the partial reversal caused by complete swelling between surface-area determinations, one concludes that some of the new bonds that remain intact at low humidities are weak enough to be ruptured by film pressure at high humidity.

The explanation just offered suggests that as the surfaces of adjacent particles are mashed together by shrinkage forces, a partial fusion of the surfaces occurs. If this is so, it indicates that as much as half of the original surface can be eliminated in this way, a fraction so high as to cast doubt on the explanation.

Irreversible Deformations of Cement Paste

Drying Shrinkage

It is a familiar fact that the first isothermal shrinkage caused by drying is only partially reversible and that subsequent cycles of wetting and drying at the same humidity are very nearly reversible. Data published by Pickett [79], are typical. This phenomenon is apparently a manifestation of the same instability that was reported in terms of decrease in specific surface area as discussed above. However, most data on irreversible shrinkage, including Pickett's, are complicated by the effects of carbonation occurring during the period of drying.

Carbonation Shrinkage

Cement gel is unstable in the presence of carbon dioxide and moisture [92]; it reacts chemically, and irreversible shrinkage accompanies the reaction. Rate of carbonation depends on ratio of surface area to volume of the specimen, permeability of the paste, internal relative humidity, and concentration of CO_2. Carbonation shrinkage is greatest when the internal humidity is about 50 percent. Practically no carbonation shrinkage occurs when the internal humidity is 100 or 25 percent. Carbon dioxide is able to react with all components of hydrated cement. The surface area per gram of original anhydrous cement appears to be slightly increased by the reaction. The mechanics of carbonation shrinkage has not yet been explained.

Effect of Externally Applied Force

A specimen of paste when subjected to an externally induced stress, such as, for example, that produced by sustained compressive force, or a bending moment, shows behavior similar to that produced by internal tension (shrinkage). Experiments of this kind are usually carried out to study plastic deformation and creep, and it is common to observe the effect of the applied load at the same time that shrinkage is going on. Experiments done under less complex conditions were reported recently by Glucklich [84]. He used sealed specimens of neat cement subjected to a bending moment. Although a small amount of leakage through the seal, and self-desiccation [66] no doubt resulted in some internal tension, the internal tension was probably moderate and relatively constant throughout the experiment. Repeated loading showed marked permanent set on the first loading, and a little on the second, but further repetitions showed reversible visco-elastic deformation. Thus it appears that the external force produced the same kind of effect as did the internal stresses induced by drying.

9. Strength

Werner and Giertz-Hedström [93] were apparently the first to observe that strength of cement paste and concrete should be a function of the concentration of hydrated cement, although the earlier cement-space ratio of Féret (1897) certainly implied such a relationship. Others who dealt with similar ideas were Work and Lasseter (1931), Woods, Steinour, and Starke (1932), Freyssinet (1933), Eiger (1934), Bogue and Lerch (1934), and Lea and Jones (1935), all mentioned by Giertz-Hedström in his 1938 review [94]. In 1947 Shinohara, [95] and Powers and Brownyard [96] independently published work based on similar ideas, and about the same concepts were used by Taplin [68] in 1959. In a dissertation published in 1953, Dzulynsky published a study of strength in relation to cement hydration in which ideas similar to those reviewed about were developed [97]. Strength was considered to be a function of γ such that

$$\gamma=\frac{C_h}{C_h+W_e+v}. \tag{48}$$

In terms of the notation used in this review,

$$C_h=(c_{hc}v_{hc}/V)\times\text{Constant}.$$

Thus, C_h is the volume of hydrated cement (not volume of gel) per unit volume of sample. W_e is the volume of evaporable water in a unit volume of specimen, whether the specimen is saturated or not, and v is the air-filled space. The indicated constant is inserted because the method of determining fixed (nonevaporable) water used by Dzulynsky was not the same as that on which c_{hc} is based.

From experimental data obtained from tests on pastes and mortars, Dzulynsky concluded that

$$R'_{\gamma}=R'_0 e^{k\gamma}. \tag{49}$$

Where R'_{γ} is the observed strength, and R'_0 and k are empirical constants. Adopting this form of empirical equation had the unfortunate consequence that when $\gamma=0$, $R'_{\gamma}=\mathrm{R}'_0$ instead of 0 as it actually is.

Powers and Brownyard [96] adopted the term gel-space ratio analogous in concept to the Feret cement-space ratio. They carried out measurements that gave compressive strength and factors proportional to the amount of gel, and arrived at the following empirical equations that represented the data very well.

$$f_c=M[(V_m/w_0)-B]=M[k(w_n/w_0)-B] \tag{50}$$

where f_c is compressive strength; M, B, and k are constants for a given cement, k being the ratio, V_m/w_n. Since the cement gel produced from a given cement has a characteristic specific surface area proportional to V_m/V_g, where V_g is the volume of cement gel, the quantity of gel in a unit volume of specimen is properly represented by V_m/V_p, where V_p is the volume of the paste. The space initially available to gel is proportional to w_0. However, since the ratio of V_m to w_0 is not literally proportional to the gel-space ratio, Powers later [98] used the function

$$X=\frac{\text{gel volume}}{\text{gel volume}+\text{capillary space}}$$

where X is the gel-space ratio. Another relationship was proposed [72] such that

$$X_F=\frac{\text{gel volume}}{\text{gel volume}+\text{capillary space}+\text{air voids.}}$$

Experimental data conformed closely to an equation of the following form:

$$f_c=f^{\circ}_c X^n \tag{51}$$

where f°_c and n are empirical constants. Since X is a fraction between 0 and 1, X^n operates as a reduction factor on f°_c. The intrinsic strength of the gel thus seems to be represented by f°_c, although when aggregate is present it probably includes other factors.

Different methods of expressing X have been given [72,98]. The following is perhaps the most convenient expression.

$$X=\frac{N}{1+\frac{1}{m}\cdot\frac{v_w}{v_c}\cdot\frac{w_0}{c}} \tag{52}$$

As seen in eq (37), N is the volume of gel produced by 1 cc of cement. Constants evaluated from data published by Powers and Brownyard are given in table 11. Calculations for X were based on values of w_n obtained by the magnesium perchlorate method. When X is based on w_n determined by the dry ice method, the values of n come out about 12 percent higher, averaging about 3.0.

Table 11. *Compressive strength functions for mortars made with five different cements*

(Data from reference 17, tables 6-1 to 6-6)

Cement No.	Calculated compound comp., %					N of eq (37)	n of eq (51)	f°_c lb/in²
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$			
14930J	22. 7	55. 8	6. 1	9. 8	2. 64	2. 15	2. 53	18, 500
15007J	48. 0	29. 1	6. 8	10. 5	2. 22	2. 18	2. 86	17, 500
15011J	45. 1	29. 1	6. 7	10. 5	2. 43	2. 18	2. 44	16, 000
15013J	39. 0	29. 0	14. 0	7. 0	3. 00	2. 18	3. 08	13, 000
15365	45. 0	28. 0	13. 3	6. 7	4. 22	2. 24	2. 68	13, 800

The figures in the last column considered in connection with the chemical compositions of the cements indicate that cement gels low in C_3A are stronger than those high in C_3A. Although there is such evidence that the strength of cement gel is a function of its chemical composition, there is no evidence that some of the chemical species present do not contribute to strength. By means of a simple demonstration, Czernin made it clear that the physical state of the solid material may be responsible for strength [99]. He demonstrated (A) that a mixture of 100 g of coarse quartz and 20 g of water was without strength, (B) that when the quartz was pulverized to "cement fineness", the same proportions exhibited some strength and (C) that when the quartz was pulverized so as to have a surface area of 20,000 cm²/g, a cylinder molded with the aid of a press could support more than a 10 kg load. Czernin remarked that in cement paste the surface area is not 20,000 but 2,000,000 cm²/g and thus ". . . the high strength attained by the cement in time is entirely plausible." Such strength is presumably due to the proximity of surfaces and van der Waals forces, as discussed in section 7. Since all the major components of hydrated cement are found in substances having high specific surface area, all contribute to at least the van der Waals source of strength. On the other hand, it seems unlikely that the strength of cement gel is due exclusively to physical forces. For reasons already given, it seems probable that there are many points of chemical bonding between the particles. Whether or not all chemical species contribute to this source of strength cannot be said. As to the relative importance of the two sources of strength, one can only speculate. When a specimen of cement paste is dried in such a way as to avoid excessive stresses during drying, the specimen becomes stronger as its evaporable water is lost; in fact, if some of the chemically combined water is removed, there is gain in strength. In terms of van der Waals forces, this gain of strength could be accounted for in terms of the reduction in average distance between surfaces in the cement gel. There is evidence also that new chemical bonds may be formed during the process of drying (see section 8).

Effect of Temperature of Curing

Ludwig and Pence [51] cured specimens of cement paste at various temperatures, measured the nonevaporable water contents, the surface area of the solids, and compressive strengths, and obtained the results shown in table 12. The relationship between gel-space ratio and compressive strength for curing temperatures 27, 66, and 93 °C conform to eq. (51) with $f_c^\circ=12{,}000$ and $n=3$. At the two highest temperatures, the strength is only 30 percent of that to be expected from the calculated gel-space ratio.

Table 12. *Effect of temperature of curing on compressive strength*

(Ludwig and Pence, 1956)
Curing time: 7 days; Nominal w/c=0.46
Cement: ASTM Type I

Temperature of curing		Pressure in autoclave	Surface of solids [a] m²/g	$\left(\frac{w_n}{c}\right)_8$	Gel-space ratio (approx)	Compressive strength, psi
°F	°C					
80	27	1 atm	103	0.142	0.68	3825
150	66	1 atm	123	.162	.79	[b] 6141
200	93	1000 psi	75	.152	.76	5,086
260	127	1000 psi	30	.139	.71	1,281
320	160	1000 psi	9.4	.139	.71	1,330

[a] Including unhydrated cement.
[b] Cured at 140 °F.

10. Permeability of Saturated Paste to Water

Under proper experimental conditions, it can be demonstrated that the flow of water through hardened cement paste complies with d'Arcy's law. To obtain a correct result, the test specimen must be completely saturated, and osmotic pressure developed in the apparatus during the test must be practically constant [100]. This observation of compliance with d'Arcy's law is the beginning point of analytical studies of permeability.

Theories of Permeability

Powers and Brownyard [101] attempted to deal with the flow of water through mature cement pastes in terms of the Kozeny-Carman concepts, as had been done previously for fresh pastes. (See section 2.) According to this approach to the problem

$$K_1=\frac{\rho_f g}{\eta_0(T)k\sigma^2}\,\frac{\epsilon_e^3}{(1-\epsilon_e)^2}\text{ cm/sec.} \qquad (53)$$

The constant k is the Kozeny-Carman constant, embodying a "tortuosity factor" and a shape factor, and σ is specific surface area of the solid particles, cm²/cc. The subscript, e, on porosity, ϵ, indicates that the effective porosity is not necessarily equal to all the space occupied by evaporable water. That is, it was known from Carman's work with clay [102], and from the work on fresh cement paste, that some of the fluid might be "immobile". Powers and Brownyard assumed that the quantity of immobile fluid would be proportional to V_m and obtained the following expression:

$$K_1=(7.85\times10^{-12})\,\frac{\rho_f g}{\eta_0(T)k}\,\frac{V_m}{V}\left[\frac{w_e}{V_m}-k_1\right]^3\text{cm/sec.} \qquad (54)$$

The numerical coefficient is the reciprocal of the square of the proportionality between V_m and surface area. k_1 is the amount of "immobile" evaporable water, expressed as a multiple of V_m. As will be seen further on, there is evidence that all the evaporable water is mobile.

Powers and Brownyard assumed that the capillary space in paste is in the form of an interconnected system of capillary channels throughout the gel, and that the hydraulic radius of the principal conduits could therefore not be calculated from the total porosity and total internal surface area. Later, Powers and Copeland nevertheless applied the Kozeny-Carman relationship to mature pastes having capillary porosity, seemingly with some success, but that approach was eventually abandoned in favor of another based principally on Steinour's adaptation of Stokes' law to concentrated suspensions, discussed in section 2. Powers, Mann, and Copeland finally arrived at eq (55) [56].

$$K_1=\frac{B}{\eta_0(T)}\cdot\frac{\epsilon^2}{(1-\epsilon)}\cdot\exp-\left[\left(\frac{\alpha}{T}-\gamma\right)\left(\frac{1-\epsilon}{\epsilon}\right)\right] \qquad (55)$$

where

$$B=\frac{\zeta(c)\,\rho_f g d_s^2}{27}. \qquad (56)$$

B is a constant comprising the following factors: the density of the fluid in the specimen, ρ_f; the gravitational constant, g; a function of particle shape, the Stokes diameter, d_s; and the number 27 which comprises the numerical constant in Stokes' law for the free fall of spheres, and another function of concentration $\zeta(c)$ introduced by Hawksley [103] which corresponds to the Kozeny-Carman tortuosity factor. The term $\eta_0(T)$ is the normal viscosity of water at temperature T. In the exponential term, $\alpha/T((1-\epsilon)/\epsilon)$ is a correction term applied to normal viscosity, and $\gamma((1-\epsilon)/\epsilon)$ was thought of as a temperature-independent factor of the same kind. The values of the constants in eqs (55) and (56), derived from experimental data, were reported as follows:

$$B=(1.36\pm 0.1)\times 10^{-10}$$
$$\alpha=1{,}242\pm 133$$
$$\gamma=0.7\pm 0.5.$$

The fit seemed good except that γ was not significantly different from zero. Powers, Copeland, and Mann, being at the time mostly interested in B, did not pursue the analysis further. Actually, the indication that $\gamma=0.0$ could only mean that the exponential term contains nothing that is independent of temperature. A review of the derivation of eq (55) showed that this might have been anticipated, particularly in the light of Hawksley's treatment. The least-squares analysis was repeated during the present writing, omitting γ, with the following results:

$$B=(1.34\pm 0.099)\times 10^{-10}$$
$$\alpha=1{,}432\pm 22.$$

The values of ϵ used in the above calculations were based on the assumption that the mean specific volume of evaporable water is independent of porosity and equal to 0.99 cc/g. (See section 3.) Based on ϵ_H, the porosity to helium, calculations gave

$$B=(1.18\pm 0.085)\times 10^{-10}$$
$$\alpha=1{,}250\pm 20.$$

The two pairs of values may be regarded as upper and lower limits. Probably the correct values are closer to those based on ϵ_H than to those based on the assumption that the specific volume of adsorbed water is 0.99.

With the success of eq (55) established, it is now clear why a Kozeny-Carman type of expression cannot be applied successfully to the flow of water in hardened cement paste. Steinour [22], experimenting with spherical particles of tapioca suspended in oil at 25 °C, showed that the Kozeny-Carman constant k is the following function of ϵ.

$$k=\frac{1}{2}\cdot\frac{\epsilon}{1-\epsilon}\cdot\exp 4.19(1-\epsilon). \tag{57}$$

For values of ϵ between 0.3 and 0.78, this equation gives $k=4.06$ within ± 0.06. This constancy, together with the limits on ϵ, accounts for the success of the Kozeny-Carman equation, and for its limitations.

For flow through cement pastes, the effects of adsorption produced a function different from eq (57). Thus, from eq (55) (without γ) and from data give above, we have

$$k_1=\frac{1}{2}\cdot\frac{\epsilon}{1-\epsilon}\cdot\exp\left[\frac{1{,}250}{T}\,\frac{(1-\epsilon)}{\epsilon}\right]. \tag{58}$$

For $T=298°\ K$, $1{,}250/T=4.19$, the same value found by Steinour. With $\epsilon=0.3$, 0.5, and 0.7, eq (57) gives $k=4.02$, 4.05, and 4.07, whereas the corresponding figures for eq (58) are 3,500, 32, and 14. Thus, for flow through pastes, k is far from constant, and its magnitude far away from that required for the success of the Kozeny-Carman equation.

The agreement between the numerical coefficients in eqs (57) and (58) is significant, and will be discussed further on.

Viscosity of Water in Saturated Paste

According to the theory of Eyring [104]

$$\eta_0(T)=A_0\exp E_0/RT \tag{59}$$

where $\eta_0(T)$ is the viscosity of water flowing under conditions that produce unperturbed patterns of flow, such as between smooth, parallel plates. E_0 is the normal energy of activation for such flow, and A_0 is a temperature-independent constant. Flow of water through hardened paste does not provide the conditions just stipulated, but, according to the same principle, the viscosity for flow through paste should be given by

$$\eta(T,a,m)=A_1\exp(E_0+E_a+E_m)/RT \tag{60}$$

where E_a and E_m denote parts of the total activation energy for flow due to adsorption (and solutes) and to mechanical interference of flow patterns, respectively. Thus, relative viscosity η^* in paste is given by

$$\eta^*=\eta(T,a,m)/\eta_0(T)=(A_1/A_0)\exp(E_a+E_m)/RT. \tag{61}$$

The exponential term in eq (55) is an empirical correction factor for normal viscosity such that

$$\eta^*=\exp(\alpha/T)(1-\epsilon)/\epsilon. \tag{62}$$

Thus

$$(A_1/A_0)\exp(E_a+E_m)/RT=\exp(\alpha/T)(1-\epsilon)/\epsilon. \tag{63}$$

The agreement pointed out earlier between the value 4.19 in eq (57), found by Steinour from experiments in which adsorption effects were absent, and $\alpha/T=1{,}250/298=4.19$, found for flow in cement paste indicates that when $E_a=0$,

$$\eta_1^*=\exp E_m/RT=\exp(\alpha/T)(1-\epsilon) \tag{64}$$

where η_1^* is the relative viscosity when there is no adsorption effect. Thus the effect of adsorption is to require the empirical function of porosity to be $(1-\epsilon)/\epsilon$ instead of $(1-\epsilon)$.

Solutions of eqs (62) and (64) are given in table 13, showing the total effect of mechanical interference and adsorption, and the mechanical effect alone.

Table 13. *Computed relative viscosity of fluid in saturated cement pastes, based on eq (63) and (64) with* $A_1 = A_0$, *and* $\alpha/T = 4.19$

w_o/c	ϵ	Hydraulic radius	Factor of viscosity increase	
			Mechanical effect η_1^*, eq 64	Total effect η^*, eq 62
		A		
0.38	0.280	7.8	20.5	[a] 47,600
.45	.346	10	15.5	2,700
.50	.395	12	12.6	600
.60	.461	16	9.6	134
.70	.489	18	8.5	78

[a] This is the value for cement gel.

Magnitude of Activation Energies

Activation energies for flow through different pastes ranged from 8,160 for $\epsilon = 0.414$ to 6,200 for $\epsilon = 0.572$, in calories per mole of water. The mean activation energy for flow of water under normal circumstances is about 4,490 cal/mole. Thus, $E_m + E_a$ ranges from about 3,700 to 1,800 cal/mole for the range of ϵ given.

General View of Factors Determining Permeability of Saturated Paste

Figure 4 is a simplified version of a diagram published by Powers, Copeland, and Mann [105] showing the principal factors controlling permeability to water at constant temperature. Line E represents the permeabilities of fresh pastes over the range of water-cement ratios indicated by the top scale, the permeabilities having been determined from bleeding rates. The resistance to flow depends on the size, shape, and concentration of cement particles, and on the effect on the particles of the initial chemical reactions (see section 2). Since the effect of adsorption on the viscosity of water in fresh paste is negligible, the scale of abscissas should have been in terms of $1-\epsilon$ instead of $(1-\epsilon)/\epsilon$. However it was not feasible to combine both functions in the same graph, and the present plotting serves the purpose.

Line A represents the permeabilities of pastes containing completely hydrated cement, and from which all alkali had been leached. The resistance to flow is determined by the size, shape, and concentration of the particles composing hydrated cement, and by the effect of adsorption on viscosity of water in paste. The marked points along line B represent a sample of paste at various stages of hydration from the fresh to the fully mature state, the final point being calculated and the rest experimental. Points along line C are the same for a different water-cement ratio. The dashed lines are estimated curves for other water-cement ratios.

Continuous and Discontinuous Capillaries

The water-filled space in *fresh* paste constitutes a continuous, interconnected system of capillaries. Production of cement gel at first constricts the capillaries without destroying continuity, but finally may divide them into segments that are interconnected only by gel pores. This transition, in terms of changes of permeability, is shown clearly by curves B and C and by dashed lines for other water-cement ratios. Capillary continuity is indicated by any point between E and A. At some stage of hydration of a given paste the point will just fall on line A, and, if there is still a reserve of unhydrated cement, subsequently produced points will follow line A. If the water-cement ratio is too high, complete hydration will not produce enough gel to destroy capillary continuity, and the terminal points fall above line A, along some such curve as D. For the particular cement represented by these points (ASTM Type I, 1800 cm²/g, Wagner), capillary continuity does not disappear at full maturity if w_0/c is greater than 0.7.

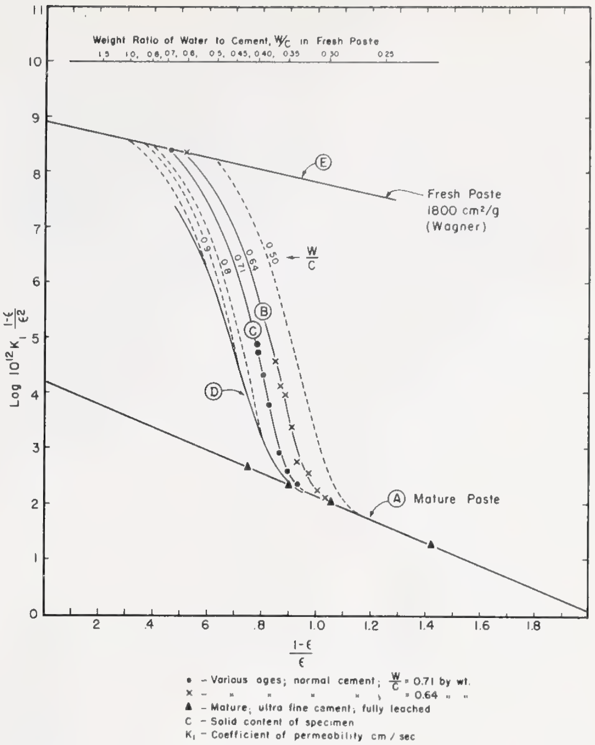

Figure 4. *Permeability functions for fresh, hardening, and mature pastes.*

Effect of Cement Composition

Differences in chemical composition of cement do not have much effect if the tests are made when the different cements are at comparable stages of hydration [100]. Data given in preceeding sections showing that the quantity and physical characteristics of cement gels produced by different cements are similar would lead one to expect this result. At early ages, pastes made with a slow-hardening cement will of course have relatively high permeability.

Effect of Alkali

Solutes in the evaporable water, particularly NaOH and KOH, reduce the rate of flow through paste by increasing the viscosity of water. Specimens from which alkali has been leached show as much as six times the permeability of companion specimens containing a small amount of alkali. When plotted in figure 4, points representing specimens containing alkali fall below line A, except for specimens having capillary continuity. Verbeck [106] found that a given cement paste, with $w/c=0.55$, was nearly five times as permeable to pure water as to a salt solution containing 12 g/l NaCl. The effect was greater the denser the paste. It seems that the effect here reported is due to the presence of hydrated cations, the effect per ion being greater the greater the degree of hydration of the ion.

Effect of Cement Fineness

The higher the specific surface of the cement, the farther to the left curve D will be, that is, the higher the water-cement ratio at which capillary continuity can be "cured out". This seems to be the only way in which the fineness of portland cement, per se, influences the permeability of mature paste.

Effect of Curing

As is apparent from figure 4, the change in permeability accompanying the transition from fresh to mature states is enormous. For example, at $w_0/c=0.7$, fresh paste is 3 million times as permeable as mature paste, 2×10^{-4} vs. 6×10^{-11} cm/sec.

It is to be expected that if the temperature of curing is high enough to increase the size of the primary particles, permeability to water will thereby be increased. Ludwig and Pence measured the permeabilities of pastes cured under water at elevated temperatures with the result shown in figure 5 [51]. Verbeck reported results of the same kind [92].

Effect of Drying

If a specimen becomes dry at some time before a permeability test, its permeability to water is thereby increased. There are not many data on this point. In one experiment, mature specimens were dried very gradually to equilibrium with 79 percent relative humidity, and then slowly resaturated, first in humid air and then in water. The coefficient of permeability was found to be about 70 times what it would have been had the specimens not been given the drying and wetting treatment. This is probably another aspect of the structural instability of cement paste discussed in section 8.

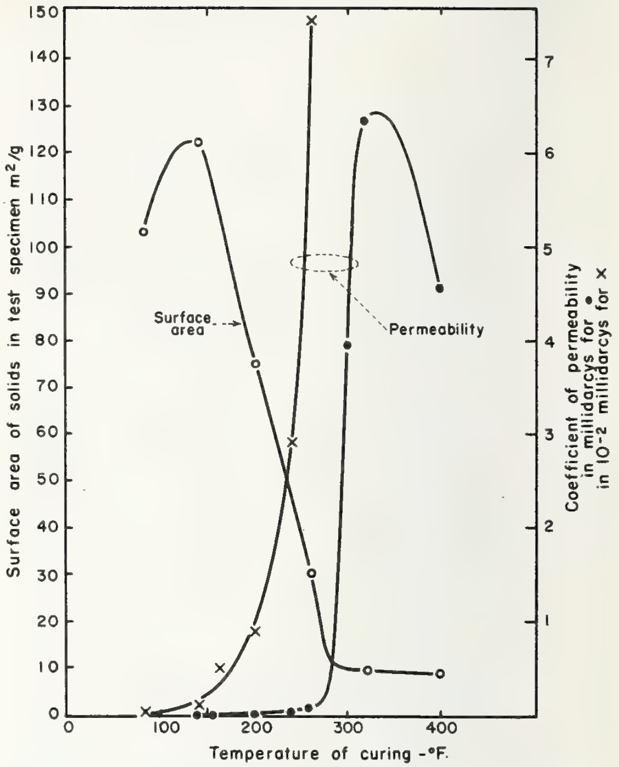

FIGURE 5. *Effect of temperature of curing on permeabilities of water-cured pastes (Ludwig and Pence).*

w/c=0.46 (nominal); cement ASTM Type I. All specimens cured under water for 7 days at temperature≥200°F; the pressure was 300 psi.

Permeability of Unsaturated Paste

Not much systematic study of movement of moisture through unsaturated paste has been reported. Powers and Brownyard [101] gave a relationship between the coefficient of permeability of a saturated specimen and a "coefficient of absorptivity" of a dry specimen, but, as the relationship was stated, it is applicable only to specimens containing an interconnected system of capillaries. It has been pointed out [105] that the "water-vapor permeability" is not ordinarily a process of transmitting vapor as such. Once water vapor is in cement paste, practically all of it is adsorbed and the transmission occurs in the adsorbed or capillary-condensed state. The motive force is not the vapor pressure difference, but the gradient in film tension discussed in section 7

Appendix 1

Glossary

To understand some parts of the text, the author's definitions of a few terms must be kept in mind. These terms are given below. (All terms defined in the glossary are italicized.)

Capillaries, or Capillary spaces: in fresh *cement paste*, the space occupied by water; in mature paste, the *pore* space in a specimen of paste in excess of about 28 percent of the volume of the specimen. These spaces are regarded as discontinuities in a mass of *cement gel.*

Capillary cavities: capillary spaces that are isolated by *cement gel.*

Cement: portland cement in the initial, practically anhydrous state.

Cement gel: the cohesive mass of *hydrated cement* in its densest state. It includes *gel pores*, and has a porosity of about 28 percent. The solid material is composed mostly of *colloids*, but noncolloids, particularly calcium hydroxide, are included in this definition. Its overall specific volume is about 0.567 cc/g dry weight; when prepared at room temperature its specific surface area is about 210m^2/g dry weight.

Cement paste: the term is applied at any stage of hydration. As applied to fresh paste, it is the mixture of cement and water, exclusive of air bubbles, if any; as applied to hardened paste, it is the rigid body produced by cement and water, composed of *cement gel, capillary spaces*, if any, and residual cement, if any. When there is neither capillary space nor residual cement, *cement paste* and *cement gel* are identical.

Colloid: a substance in such physical state that its chemical and physical properties are influenced to a significant degree by the surface energy of the substance. A solid colloidal substance may be amorphous or crystalline, but, if crystalline, the crystals are apt to be imperfectly organized. A colloid is characterized by a high specific surface area. In *cement gel* calcium hydroxide, and perhaps some other components are not colloidal.

Dry ice method: the method of isothermal drying of samples of *cement paste* described by Copeland and Hayes [36]; referred to also as the Copeland and Hayes method.

Gel: a cohesive mass of colloidal material. (Compare with *cement gel.*)

Gel pores: the pores in *cement gel.*

Hydrated cement: a collective term for all the chemical species produced by the reactions between *cement* and water, except transient products of initial reactions.

Magnesium perchlorate method: the method of isothermal drying of samples of *cement paste* described by Powers and Brownyard ([17], pp. 249–336) and by Powers [98], now largely supplanted by the *dry ice method.*

Pore (in *cement paste*)*:* space in *cement paste* that is, or can be, occupied by evaporable water. Its definition, quantitatively, involves a standard method of drying the sample.

Appendix 2

List of Repeatedly Used Symbols

c = weight of cement in its original state, grams.
c_h = weight of original cement that has become hydrated.
c_i = weight of cement after being ignited.
h = relative humidity $= p/p_s$ where p is the existing water-vapor pressure and p_s is the water-vapor pressure at saturation and same temperature.
ln = logarithm to the base e.
log = logarithm to the base 10.
m = maturity factor = fraction of cement that has become hydrated.
N = volume of cement gel produced from 1 cc of cement.
P = pressure, either positive or negative.
P_C = pressure in capillary water (usually negative).
v_c = specific volume of cement, cc/g dry weight.
v_e = specific volume of evaporable water, cc/g.
v_g = specific volume of cement gel, cc/g dry weight.
v_{hc} = specific volume of hydrated cement, cc/g dry weight.
v_n = specific volume (apparent) of nonevaporable water, cc/g.
v_p = specific volume of saturated paste, cc/g saturated weight
v_t = specific volume of total water in saturated specimen, cc/g.
v_w = specific volume of water under existing pressure, cc/g.
v_w° = specific volume of water under reference pressure, cc/g.
V = volume of specimen or batch of paste.
V_m = the Brunauer-Emmett-Teller surface-area factor = weight of water required for a monomolecular adsorbed layer on a sample dried by the dry ice method of Copeland and Hayes [36]. (See glossary).
$(V_m)_8$ = ditto for a specimen dried by the magnesium perchlorate method ([17] pp. 249–336).
w = weight of water in fresh paste.
w_o = ditto, corrected for water displaced by bleeding.
w_i = the immobile water factor.
w_n = nonevaporable water = water retained by a specimen prepared by the dry ice method of Copeland and Hayes [36].
$(w_n)_8$ = nonevaporable water = water retained by a specimen of paste prepared by the magnesium perchlorate method, vapor pressure 8μ of mercury. ([17] pp. 249–336).
ϵ = porosity, ratio of volume of interstices to gross, overall volume of a material.
ϵ_C = capillary porosity.
ϵ_H = porosity as calculated from the volume of the saturated specimen and the specific volume of the dried solid as determined by displacement of helium.
ρ_c = density of cement, g/cc.
ρ_s = density of solid, g/cc.
ρ_f = density of fluid, g/cc.
σ = specific surface area, cm^2/cc.
Σ = specific surface area, cm^2/g.

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Discussion

H. W. W. Pollitt

My remarks concern Mr. Powers' most interesting paper. I should like to say first how much

I agree with him that there is a need for a closer connection between chemical and physical studies of cement and concrete. Particularly welcome from this point of view was the paper in Session II by Welch and Gutt, who discussed the effect of impurities on cement strength. It is by virtue of physical properties such as strength that cement is used in practice so that cement chemistry is chiefly of importance insofar as it can be related to the physical properties of cement.

Returning now to Mr. Powers' paper, I should like to comment on the section dealing with permeability where it is said that the presence of dissolved alkalis in water materially affects its penetrating power and it is remarked that this may be due to viscosity effects.

We, at the Associated Portland Cement Manufacturers Research Department, have some evidence that factors other than viscosity may be important. As everyone present will know, contractors frequently make concrete with insufficient strength which is usually due to too high a water-cement ratio. It is, however, common practice on the part of the contractor to assert that the cement is bad. In self-defense we have developed a method of determining in hardened concrete what was the water-cement ratio at the time of setting.

The procedure is to dry a piece of concrete at 105 °C to constant weight and to place it after cooling in carbon tetrachloride under vacuum. The space left by evaporated water is measured by the amount of carbon tetrachloride absorbed. Normal chemical analysis determines the quantities of cement and of combined water so that the total water and water-cement ratio at the time of setting can be calculated. The method works well, giving usually an accuracy of ± 0.02 and often ± 0.01.

During the research which led to the development of this test, several liquids were investigated and the effects of entrained air and honeycombing were studied. It was found that carbon tetrachloride would fill the water voids but not enter the air voids, whether these were due to entrained air or to honeycombing, except when large open voids were visible in the surface of the specimen. In that case any carbon tetrachloride taken up by the open voids drained out when the specimen was removed from the carbon tetrachloride. Pure water on the other hand explored a larger volume than did carbon tetrachloride, presumably by penetrating into air voids. When lime water was used the volume of it absorbed by the specimen was intermediate between those for pure water and carbon tetrachloride respectively; the greater the concentration of lime the less the volume absorbed.

Now the viscosity of carbon tetrachloride is very close to that of water. It therefore appears that in dry hardened concrete the water voids are penetrable by fluids having the viscosity of water. This is consistent with the concept of a network of interconnected capillaries. The air voids on the other hand are penetrated by water, rather less by lime water, and not at all by carbon tetrachloride. This suggests that an air void is surrounded by a membrane which is impermeable to an inert fluid having the viscosity of water but permeable to water to an extent depending on its content of dissolved lime. The clear inference is that it is the dissolving power of the fluid with respect to the membrane that governs the degree of penetration into air voids.

It seems possible that chemical reactions may similarly have affected the results reported by Mr. Powers. It is conceivable that precipitation of lime occurs when water containing alkalis passes through capillaries in cement paste and that the precipitate constricts the capillaries and opposes flow.

I should be interested to have Mr. Powers' comments on these facts and opinions.

Discussion

G. E. Bessey

Compared with the complexity of hydraulic cement concrete and cement pastes, the more simple hydrous calcium silicate bonded products, sand-lime bricks, formed by direct reaction of well-compacted mixes of lime and silica in high pressure steam, offer a clearer picture. From all the information now available, as described in various papers presented at the Symposium and from the writer's experience with the industrial products, it seems that the initial reaction in their hardening is normally to form "amorphous" CSH, which slowly converts to a tobermorite phase, and at the higher pressures and still longer times may convert to xonotlite. Determinations of the combined lime and "soluble" silica in a large number of commercial bricks show ranges in lime:silica ratio of only 0.78 to 1.28 with over two-thirds of the analyses between 0.9 and 1.2. Bearing in mind that the calculated ratio involves the combined error in each instance of four separate analytical determinations, the ratio is remarkably constant.

In these materials the water content used in pressing is low, and insufficient to fill the voids in the pressed brick. Consequently strength is independent of water-binder ratio and bears a simple linear relation to the binder (i.e., lime) content over the practical working range.

It is perhaps more interesting in relation to the position with cement products that the drying shrinkage, other things being equal, is similarly related almost linearly to lime content over the practical range.

When the ratio of lime to silica is increased further, beyond the range used in practice, the available surface of silica becomes saturated and a dicalcium silicate hydrate is formed. This is a less effective bonding agent and has also, it seems, lower drying shrinkage, so that the curves of both

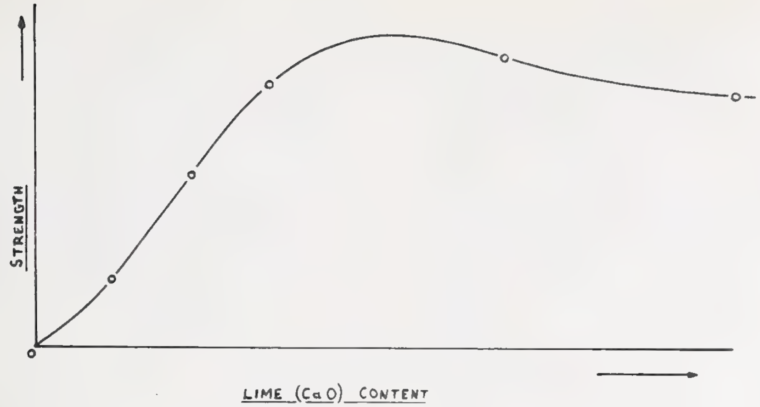

Figure 1. *The effect of lime content upon strength of hydrated calcium silicate bonded (sand-lime) bricks*

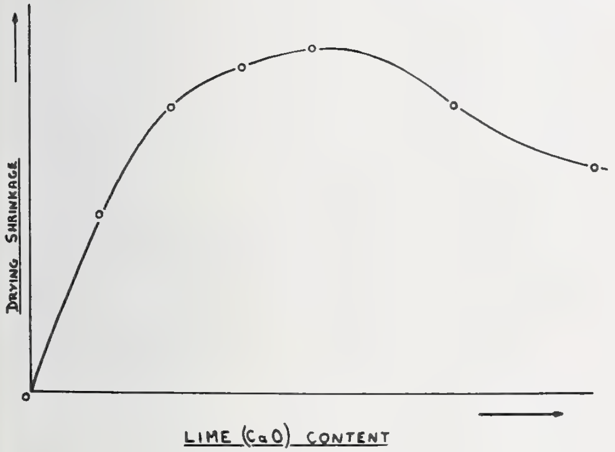

Figure 2. *The effect of lime content upon drying shrinkage of hydrated calcium silicate bonded (sand-lime) bricks*

strength and drying shrinkage versus lime first depart from rising linearity and then drop. This is shown in figures 1 and 2, which are reproduced from actual data using a particular sand with the curves passing through all the experimental points. Since the actual values for given lime contents, and the contents at which inflection of the curve takes place, are dependent upon the fineness of the sand, and other factors, the values are not shown on either axis. The form of curve remains the same for all sands.

Closure

T. C. Powers

In his remarks entitled "A Few Unsolved Problems of Cement Hydration", Mr. Czernin raises some questions that deserve careful consideration. One of the questions exemplifies a difficulty confronted by every writer on this subject. The difficulty is that concrete is not a substance that can be described in terms of a few single-valued characteristics—far from it. Several of its important properties may have any one of a wide range of characteristic values, and these various values may appear in one or another of innumerable possible combinations. Furthermore, different parts of a single specimen may show significantly different characteristics. For such reasons, a statement that is true about the characteristics of a particular specimen, or class of specimens, of cement paste or concrete is liable to be untrue if applied generally.

Mr. Czernin cited data showing that cement paste becomes progressively firmer throughout the period we have called dormant. Such behavior is typical of pastes in which the cement grains are initially very close together. Such a paste might have standard, "normal", consistency and a water-cement ratio of about 0.23. It would not bleed, and cementation probably would begin immediately, producing the stiffening reported by Mr. Czernin. On the other hand, if a paste is initially soft enough to bleed, the cement grains are well separated by water, and they remain separated throughout the dormant period, except in the sediment that accumulates on the bottom of the container. The bottom part stiffens, just as does a paste having a high particle concentration at the start, but the upper part of the sample, which bleeds at constant rate, does not undergo cementation, and its consistency does not change very much until the period of set begins.

Thus, Mr. Czernin's argument on this point is right or wrong depending on whether or not one speaks of a paste in which the cement particles are highly concentrated . The point to be emphasized is that setting and cementation depend upon physical factors as well as chemical ones, and what is true about one class of pastes may not be true about another class.

Another question raised by Mr. Czernin pertained to the mechanics of hydration. This bears on the concepts of gel structure and the evolution of that structure dealt with in section 6 of my paper. There is a natural tendency to endow a mental picture of the structure of cement paste with simplicities not required by the basic concept on which the picture is based. It is not necessary to suppose that cement gel grows in such way as merely to translate outward the original contours of each cement grain, thus maintaining a clear demarcation between cement gel and capillary space. Mr. Czernin's excellent pictures as well as many other observations, show that, at least in the early stages, cement gel does not grow that way. At the start, gel substance seems to be deposited on any solid surface that is itself not producing gel. In concrete, such surfaces would be presented by aggregate particles and calcium hydroxide crystals formed early in the process. Since gel substance is insoluble, it cannot remain in solution very long; it seems, therefore, that the development of gel one sees at considerable distances from the source material is the result of surface diffusion, the gel substance being essentially in the adsorbed state until it reaches a place where gel particles can grow.

Regardless of where the gel substance is produced, it cannot achieve a density that averages more than about 0.72 cc of solid per cc of space. When any region becomes filled to this degree, we say that the region is full of cement gel.

I have dealt with this question in considerable detail in a paper prepared for the January 1961 issue of the Journal of the PCA Research and Development Laboratories. The arguments in that paper lead to the conclusion that no single term derived from other contexts, such as solution-and-precipitation, or topochemical reaction is able to designate adequately the complex process by which cement becomes hydrated.

Mr. Czernin's final comment pertains to the matter of gel porosity; he refers to a "theory of constant gel porosity." Actually, I know of no theoretical basis for predicting that the porosity of the heterogeneous mass of hydration products should be always the same when excess cement is present regardless of the amount of excess. Without such a theory, we can only say that this has been observed to be true, within the error of the experimental determinations, as shown in figure 1 of my Symposium paper. Mr. Czernin argues, "If the porosity of the hydrated part remains the same, whatever the amount of unhydrated material distributed in the gel, then the strength should remain at the same level or at least near it when we lower the w/c from 0.4 to the lowest possible ratio." This is a logical argument based on the tacit assumption that the strength of a specimen of cement paste depends only on the porosity of the hydrated part of the paste. However, I do not know of a theoretical basis for such an assumption, and it seems contrary to observation. As Mr. Czernin said, we know that even though the porosity of the hydrated part of specimens is the same when different amounts of excess cement are present, strength is higher, the higher the excess cement content. It seems therefore that we must conclude that gel strength alone does not define strength of a specimen of paste. Also it is probably true that when different cements are compared, gel porosity is not the only factor determining the strength of gel itself. The empirical relationship between strength and gel-space ratio is more general than the relationship between strength and water-cement ratio, but it nevertheless has limitations and uncertainties common to most empirical relationships.

Dr. Bessey's remarks and data bring out a point about empirical strength relationships that is sometimes overlooked. The point is that in concrete, air voids have about the same weakening effect as an equal volume of the much smaller capillary spaces in the hardened paste. This means that void-size does not have much effect on strength. The same seems to be true of pressed, sand-lime brick. Before curing, the spaces between sand grains are filled with three components: air, water, and lime. After curing, some of the water-filled space has become filled with reaction product, and thus the total volume of voids becomes the sum of the volumes of the original air-filled spaces and the residues of originally water-filled spaces. If the water content of the interstitial space is varied while holding the amount of reaction product constant, the effect is to change the ratio between the volumes of the two classes of voids. Dr. Bessey's statement indicates that such a change does not affect the strength, if the properties of the hydration product remain the same.

Mr. Pollitt referred to the remark that alkalis "reduce the rate of flow through paste by increasing the viscosity of water . . . ." This observation pertained to the rate of flow *through* a saturated specimen in a permeability test. The corresponding effect on rate of penetration of a dry specimen was not tested. I should like to suggest that viscosity is not likely to be a factor in the phenomena discussed by Mr. Pollitt. Viscosity affects the rate of flow under a given driving force, but not necessarily the amount of fluid that a given specimen can hold. Water in gel pores seems to have a very high viscosity, perhaps 50,000 times the normal value (table 13) and yet it penetrates dry gel readily. The same forces that affect viscosity also pull the water molecules into dry gel.

Mr. Pollitt's observations pertaining to the penetration of dry concrete by different fluids brings to mind certain experiments we reported in 1947. (Proc. Am. Concrete Inst. **43,** 693, 1947, tables 5–11; Research Lab. Portland Cement Assoc., Bull. 22, p. 693.) These experiments had to do with the determining of the specific volume of dry hydrated cement in the form of small granules obtained by crushing and sieving hardened paste. The granules were free from air bubbles and the like. Being incomplete, the data do not permit direct quantitative comparison between the results obtained in carbon tetrachloride and in water, but it is nevertheless clear that the apparent specific volume of dry hydrated cement is considerably higher in organic liquids than it is in water. The following table illustrates the point.

Apparent Specific Volume of Hydrated Cement (*Cement 20Q*)

Displacement fluid	Molar volume, (temp. 23°)	Relative molar volume	Apparent specific volume of hydrated cement
	cc		*cc/g*
Water	18	1.0	0.395
Acetone	73	4.0	.408
Toluene	106	5.9	.429

The apparent specific volume depends mostly on the degree to which the fluid used in the experiment is able to penetrate the capillary spaces and gel pores in each of the granules of the sample, and to the degree to which the specific volume of the fluid is influenced by adsorption. The subject is discussed briefly in the third paragraph of section 3 of my Symposium paper.

As pointed out in the Symposium paper the mean width of gel pores is estimated to be about 5 times the diameter of a water molecule. Since the carbon tetrachloride molecule is about 5.3 times as large as the water molecule, and since also carbon tetrachloride cannot cause the gel to swell appreciably, it is not surprising that carbon tetrachloride is unable to penetrate cement paste to the same degree as does water.

When a dried specimen of concrete is submerged in water the gel pores and capillary spaces seem to become filled readily, and it is theoretically possible for at least the very small air bubbles to become filled with water. It is our experience, however, that the time required for an appreciable amount of water to enter air bubbles or any voids of that kind is very long as compared with the duration of an ordinary laboratory experiment. Indeed, the effectiveness of entrained air in protecting the cement paste in concrete from frost action out of doors can be considered practical evidence that air voids do not become filled with water under ordinary circumstances. It seems, therefore, that the differences in penetration found by Mr. Pollitt are probably due to differences in size of molecule and degree of swelling, and probably not to a difference of penetration into air voids.

It does seem likely that the solubility of lime and alkali compounds in water should make more space available to water than to a fluid in which these salts are insoluble. Similarly, an aqueous solution of lime should find less space than pure water. However, considering the solubilities and quantities involved, it seems unlikely that this factor could be large. The amount of difference between absorption of pure water and lime water observed by Mr. Pollitt was not stated.

Paper V–2. The Microstructure of Hardened Cement Paste*

Åke Grudemo

Synopsis

The review covers not only the microstructures of hardened paste products but also the formation of lattice structures and the crystal habits of various compounds related to cement hydration in general, and represents a compilation of available data obtained especially in electron-optical studies.

Experimental methods of studying colloidal structures are reviewed briefly, with particular reference to the use of electron microscopy and electron diffraction in the examination of cement hydration products.

Different types of compounds appearing in the hydration of portland cement are reviewed separately with respect to their microstructural properties, starting with various modifications of lime hydrate.

In dealing with the hydrated aluminate and aluminoferrite phases, and the complex salts of the sulfoaluminate hydrate type, various possibilities of arrangement of their lattice structures are suggested. The appearance of hexagonal-plate phases of calcium aluminate hydrates in pastes is described. The problem of ettringite formation is treated in relation to some phenomena observed in cement slurries.

The general principles governing the formation of lattice structures in calcium silicate hydrates are described and illustrated by reviewing a number of crystal structures determined. The crystal habits and the principles of structure formation in tobermorite phases are treated in particular detail, as is also the problem of afwillite formation.

The hydration products of pure calcium silicates are reviewed and considered with special reference to paste-hydration processes. The experimental data from structural studies of paste-hydrated silicates are compared with corresponding observations of the gel phases in portland cement pastes. These are illustrated by a number of electron micrographs from paste samples of various description, selected in order to elucidate the influence of such factors as time of hydration, type of cement used, w/c ratio, fineness of grinding, and curing conditions.

The data obtained in structural studies of pastes are found to disagree with a number of current theories on paste microstructure. The need for a reconsideration of these theories is emphasized, and a few problems of special importance for further research are indicated.

Résumé

Le présent compte-rendu n'embrasse pas seulement les microstructures de produits en pâte durcie mais également la formation de réseaux cristallines et les modes de cristallisation de différents composés se rapportant à l'hydratation du ciment en général; ce compte-rendu est également une compilation des données disponibles obtenues essentiellement par des études optiques électroniques.

Il est brièvement rendu compte des méthodes expérimentales d'étude de structures colloidales, une attention particulière ayant été accordée à l'emploi de la microscopie électronique et de la diffraction électronique pour l'examen des produits d'hydratation du ciment.

Différents types de composés apparaissant lors de l'hydratation du ciment portland sont traités séparément en ce qui concerne leurs propriétés micro-structurales, en commençant par différentes modifications de l'hydrate de chaux.

Au sujet des phases d'aluminate et d'aluminoferrite hydraté ainsi que des sels complexes du type hydrate de sulfo-aluminate, il est proposé différentes possibilités de disposition des elements de structure dans le réseau cristalline. L'apparition des phases de plaques hexagonales des hydrates d'aluminate de calcium dans les pâtes est décrite. Le problème de la formation d'ettringite est traité par rapport à certains phénomènes observés dans les laits de ciment.

Les principes généraux régissant la formation de réseaux moleculaire dans les hydrates de silicate de calcium sont décrits et illustrés par la présentation d'un certain nombre de structures cristallines déterminées. Les modes de cristallisation et les principes de la formation de structure dans les phases de tobermorite fait l'objet d'études détaillées particulières, de même que le problème de la formation d'afwillite.

Les produits d'hydratation de silicates de calcium purs sont étudiés du point de vue spécial des processus d'hydratation de la pâte. Les données expérimentales des études de structure de silicates hydratés en pâte sont comparées aux observations correspondantes des phases de gel dans les pâtes de ciment portland. Ces données sont illustrées par un certain nombre de microphotographies électronique d'échantillons de pâte de descriptions diverses choisies dans le but de mettre en lumière l'influence de facteurs tels que le degré d'hydratation, le type de ciment utilisé, le rapport eau/ciment, la finesse du grain et les conditions de durcissement.

Les données obtenues lors d'études de la structure des pâtes sont en désaccord avec un certain nombre de théories courantes sur la microstructure des pâtes. La nécessité d'une révision de ces théories est soulignée et il est fait mention de quelques problèmes revêtant une importance particulière pour les recherches futures.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden.

Zusammenfassung

Dieser Bericht umfasst nicht nur die Mikrostrukturen von gehärteten Pasten sondern auch die Gitterstrukturbildung und die Kristallformen verschiedener, sich auf die Zementhydratation beziehende Phasen im allgemeinen, und stellt eine Zusammenfassung der, besonders durch elektronoptische Untersuchungen gewonnenen, erhältlichen Angaben dar.

Über Versuchsmethoden für die Untersuchung von Kolloidalstrukturen wird kurz berichtet mit besonderem Hinweis auf die Anwendung der Elektronenmikroskopie und der Elektronenbeugung zur Untersuchung von Zementhydratationsprodukten.

Über die Eigenschaften von verschiedenen in der Hydratation des Portlandzementes erscheinenden Verbindungen wird einzeln berichtet mit besonderer Rücksicht auf deren mikrostrukturellen Eigenheiten, wobei mit den verschiedenen Modifikationen des Kalkhydrates begonnen wird.

Betreffs der hydratisierten Aluminat- und Aluminoferritphasen sowie der zum Sulfoaluminattype gehörenden Komplexsalze werden verschiedene Möglickheiten für die Anordnung ihrer strukturellen Elemente in Gitterstrukturen vorgeschlagen. Die Bildung und Eigenschaften der hexagonalen Plattenphasen der Kalziumaluminathydraten in Zementpasten wird beschrieben. Das Problem der Ettringitbildung wird erörtert mit Bezugnahme auf einige in Zement-Wasser-Mischungen beobachteten Erscheinungen.

Die allgemeinen Gesetze, die die Bildung von Gitterstrukturen in Kalziumsilikathydrate regeln, werden beschrieben und durch eine Anzahl von experimentell bestimmten Kristallstrukturen illustriert. Die Kristallformen und die Prinzipien der Strukturbildung in den Tobermoritphasen werden besonders eingehend behandelt, sowie auch das Problem der Afwillitbildung.

Die Hydratationsprodukte von reinen Kalziumsilikate werden mit besonderer Rücksicht auf die Hydratationsvorgänge in Pasten behandelt. Die Ergebnisse, die durch Strukturuntersuchungen von reinen, in Pastenform hydratisierten Silikaten erhalten sind, werden mit entsprechenden Beobachtungen der Gelphasen in Portlandzementpasten verglichen. Diese werden durch eine Anzahl Elektronenmikrophotographien von Pasteproben verschiedener Typen illustriert, die in der Absicht, den Einfluss von solchen Faktoren wie die Hydratationsdauer, der Typ des verwendeten Zementes, das Wasser/Zementverhältnis, die Zermahlungsfeinheit und die Erhärtungsverhältnisse zu erläutern, ausgewählt worden sind.

Es ergibt sich, dass die durch Strukturenuntersuchungen von Pasten erhaltenen Angaben nicht mit einigen, vorläufig gültigen Theorien über die Mikrostruktur von Pasten übereinstimmen. Die Notwendigkeit einer erneuten Prüfung von diesen Theorien wird hervorgehoben, und einige Probleme von besonderer Bedeutung für weitere Untersuchungen werden angegeben.

Introduction

As is generally recognized by all who have anything to do with cement research, hardened cement paste is a complex and highly variable system of particles of a manifold of sizes, shapes, and compositions, of water in different states of fixation, and of pores and voids, the sizes and distribution of which depend on how the particles of solid matter are aggregated and linked to each other. It can of course be stated quite generally that the microstructural properties of this system, as well as of any multicomponent hydrate system, are functionally dependent on a number of primary variables such as, in addition to time and the thermodynamic variables (temperature and water vapor pressure), the initial chemical and mineralogical composition, the initial particle size distribution, the amount of mechanical work applied during mixing, etc. In review of the present-day knowledge of the microstructure it would therefore, strictly speaking, be necessary to consider first the fundamental theories of the processes taking place in the reaction of cement with water, and to refer to a great number of papers dealing with different aspects of the chemistry and crystallography of components within the cement hydration system.

However, since the time of the 3d Symposium on cement chemistry in London, 1952, the literature on cement has been enriched by a number of textbooks, viz. (in order of time of publication) Kühl [1],[1] the Proceedings of the London Symposium [2], Bogue [3], Lea [4], Heller and Taylor [5], and the Proceedings of the Moscow Symposium 1956 [6]. Taken together, these books provide a most exhaustive account of practically everything written on the subject of the chemistry of cement and its constituents up to 1956. In addition, the latest developments in cement research are reviewed in a series of principal papers presented at this Symposium. In the present review, therefore, only papers dealing more specifically with matters pertaining to the microstructural properties of cement-hydration constituents will be referred to and commented on in connection with the discussion of various microstructural problems.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Definitions and Nomenclature

Only materials and paste constituents within the general field of portland cement hydration will be considered in this review, and the term "cement" is used in the meaning of portland cement, if not otherwise stated.

In addition to the accepted abbreviations of chemical symbols (C–S–A–F–H), the oxide symbols $\overline{S}=SO_3$ and $\overline{C}=CO_2$ are introduced for the sake of uniformity. Further abbreviations used are EM = electron microscopy, ED = electron diffraction, and XD = X-ray diffraction.

Compounds of unknown or unspecified composition are generally denoted with dashes instead of subindices, e.g., C–S–H. Some problems of nomenclature concerning compounds within the C–S–H system still remain unsettled. The nomenclature proposed by Bogue [7] some years ago, which aimed at reconciling the various names and notations used, and at introducing a system of uniform symbols, has not been generally accepted. Some writers have preferred to use mineral names even for ill-crystallized and ill-defined products exhibiting certain structural or stoichiometric analogies to some natural mineral previously described in the literature on mineralogy. It does not seem possible, at present, to find a completely unambiguous denomination system. In the present review, Bogue's nomenclature and mineral names will therefore be used alternatively or in combination, as the case may be

Experimental Methods for Studying Microstructure

General Remarks

The subject indicated by the heading is in itself a very large one, and only a few comments will be given here, in order to clarify in some degree the present situation regarding the various possibilities of exploring the microstructures of hydrogels, or in general, systems of colloidal particles.

It should be recognized that the concept of microstructure can be divided into two distinct (although closely related) parts. First, microstructure can be considered from the point of view of crystallography pertaining to the repeat units of crystal structure, and the spatial arrangement of ions and ionic complexes within the unit cells, and studied by means of diffraction methods (XD and ED). Second, there is the morphologic aspect, involving the shape, size, and distortion of more or less well-crystallized particles, and the aggregation of such particles to condensed systems, characterized, among other things, by the nature of the interparticle links and the distribution of pores and voids, and studied in magnified images (light microscopy and EM).

It is evident that the development of ideas concerning the crystallographic aspect of cement hydration constituents is largely dependent on data obtained using analytical methods of study of a more conventional type, and related to the reaction chemistry and the phase diagrams of hydration systems which are less complex than the cement-water system.

The morphologic aspect, on the other hand, may serve to bridge the gap between pure and applied cement research, being closely related to problems concerning the physical properties of cement paste, especially its mechanism of deformation when used as a construction material in cement and concrete technology.

Crystallographic Methods

In the review of the structures of cement hydration compounds given by Bernal [8] at the London Symposium, it was emphasized that although at that time a comparatively large number of crystal structures related to the cement hydration compounds had been at least partly resolved, it would be necessary to develop essentially new XD techniques in order to attack the structures of other compounds of great interest in the field of cement hydration, especially within the C–S–H system. The reason for this, it was stated, was that most of the compounds formed in the reaction of cement with water, including hydrothermal products of autoclaving at elevated temperatures, or occurring as natural minerals, are only available as materials of a very low degree of crystallinity, consisting of small and mostly distorted crystals possessing large unit cells of low symmetry.

It seems that the situation has changed radically in this respect during the last few years. Difficulties which were at one time regarded by many crystallographers as nearly insurmountable, are at present well on their way to being overcome, due to the combined efforts of crystallographers all over the world, using refined methods of XD analysis and applying recently developed crystallochemical theories of structure formation. The most notable contributions in this field have perhaps been given by crystallographers at the University of Aberdeen and the Academies of Science of Moscow and Berlin. Some implications of the results of these studies of crystal structures for the more general problem of structure formation in cement hydration processes will be considered in later sections of this review.

In general, rational applications of standard single-crystal or powder XD techniques have proved to be sufficiently effective. However, great care must be taken to select suitable and well-defined crystal specimens for investigation, and preparation and mounting of crystals must often be executed under the microscope. Structural transformations during dehydration at elevated temperatures have been studied by *in situ* XD techniques. Electron-diffraction single-crystal diagrams have sometimes been useful in the determination of the true unit cells.

Microfocus X-ray tubes in combination with microcameras have in some cases been successfully used to improve the resolution of powder patterns and to decrease the exposure times. However, the X-ray diffractometer with Geiger-Müller tube counter and recorder units seems to have become the standard X-ray crystallographic equipment in most cement research laboratories, chiefly because of the high adaptability of this type of instrumentation for different purposes, for which either high resolution, high recording speed, or high accuracy of intensity measurements is essential. Some typical uses of the recording diffractometer are, e.g., the quantitative analysis of the mineral composition of a mixture of crystalline compounds, and the determination of particle size from small-angle scattering or line-width measurements. Other instruments which have been commonly applied in cement research in recent years, are powder cameras equipped with focusing monochromators, which are capable of resolving even the very closely spaced diffraction lines frequently appearing in powder photograms from a mixture of cement hydration minerals, especially the clinker minerals themselves, or steam-cured C–S–H mixes. The monochromator camera is superior to ordinary diffractometers for the special problem of detecting with certainty the presence of weak reflections which are, in diffractometer records, either masked by strong reflections nearby, or not clearly resolved from the background ripple. On the other hand, it would seem very difficult to avoid selective crystal-orientation effects in the very thin, and strongly compressed, powder layer samples used in monochromator cameras, which make them less suitable for measurements of relative line intensities in general, and, specifically, for a quantitative analysis of mineral composition.

It would seem that whereas different ways of using XD methods to their full capacity in examining crystal structures related to cement hydration have been well demonstrated, this is not nearly true with regard to the application of ED techniques, and major contributions to the advancement of knowledge of cement hydration processes are probably to be expected from investigators using ED methods.

Facilities for recording ED patterns are normally incorporated in different types of three-stage electron microscopes. Because of the strong interaction of electrons with matter, extremely small sample volumes can be singled out and examined by means of the so-called selected-area diffraction technique. In this way even minor constituents of a composite material can be detected and studied with respect to their diffraction characteristics. crystal symmetry, and unit cells. This possibility constitutes the main difference between XD and ED methods. An XD powder pattern of a mixture of crystals gives the superimposed patterns of different constituents with intensities proportional to their relative amounts, whereas the ED patterns vary from one point to another in a suitably prepared sample scanned with the electron beam.

The electron beam in an electron microscope is almost completely absorbed by solid matter of an effective thickness of the order of 1,000 A, which is thus the maximum particle thickness permitting ED diagrams to be obtained. This is also the upper limit rather arbitrarily set for colloidal particle size, and ED methods are therefore particularly suitable for studying structures of colloidal particles.

It is an intrinsic property of colloidal particles, if at all crystalline, to have their crystal lattices restricted in one or more directions. This restriction is equivalent to a degeneration of the points of the so-called reciprocal lattice into reciprocal density distributions of ellipsoidal symmetry. Since the ED pattern is a practically undistorted image of a section through the reciprocal lattice, the ED reflections from very small and distorted crystal elements are often observed to be diffuse or streaky. Because of the special method of preparing and mounting EM samples, crystal-orientation effects are also, as a rule, strongly pronounced. Owing to these circumstances, the relationships, as measured in XD diagrams, between stronger and weaker intensities of reflections, are often observed to be reversed or strongly changed in ED diagrams of the same sample. It can thus be stated that selected-area ED patterns can hardly be used for a quantitative determination of relative intensities in the same way as diffracted X-ray intensities are employed in electron-density syntheses.

A further consequence of the strong interaction of high-speed electrons with matter is that the sample particles will be heated when hit by the electron beam. It is mostly difficult to estimate the temperatures reached in this way, since too many uncertain factors are involved. However, under normal conditions, and when care is taken not to increase the electron beam intensity to a higher level than is strictly necessary for observing and recording the images visible on the fluorescent screen, the temperature of at least the thinner particles or particle aggregates in a sample is probably well below 100 °C.

Even these comparatively low temperatures, especially in combination with the vacuum maintained in an electron microscope or ED instrument, are still sufficient to cause dehydration and destruction of delicate or ill-crystallized hydrate structures. Crystal-structure transformations and changes in morphology are frequently observed in EM studies, and can sometimes be expected to have occurred even before the electron beam is switched on. Although in most cases the effects of heating can be considered negligible, one can never be quite certain that some unobservable change has not occurred. This circumstance is obviously a disadvantage of EM and ED techniques applied to the study of metastable and easily decomposing cement hydration constituents, since it may lead to serious misinterpretations of various observations made.

On the other hand, valuable conclusions on compounds of unknown identification can sometimes be drawn by using the technique of deliberately increasing the intensity of the electron beam successively, until a transformation of crystal structure or habit takes place and can be observed as a radical change in the ED diagram given by the substance studied.

Temperatures amounting to several hundred degrees C can be reached in this way, which is in many cases sufficient to remove all volatile oxide components from the specimen and transform it to some anhydride compound, the ED pattern of which can be used for identification and further analysis of the hydrate originally present.

The fact that the temperatures of the sample particles heated by the electron beam cannot be easily controlled or measured is evidently a disadvantage inherent in this technique, although in many cases of minor importance. In special electron-microscope constructions, the specimen stage is equipped with electric heating, or alternatively, liquid-air cooling, and a device for temperature measurement and control. It is possible that such devices will be of great use in future research on the microstructural properties of thermally unstable colloidal materials.

The commonly used XD technique of bringing out the whole spectrum of crystal reflections by rotating a specially selected crystal about one or more of its principal crystal axes cannot be employed in ED, on account of obvious difficulties of design caused by the extreme minuteness of the single crystal specimens. Disregarding the use of devices for tilting the specimen through a limited angular range [9], a single-crystal ED pattern represents a section of the reciprocal lattice, recorded for one particular, and mostly arbitrary, setting of a stationary crystal in a stationary and very nearly monochromatic, electron beam.

Because of these circumstances, and because of the above-mentioned effect of various types of lattice restrictions and distortions, single-crystal patterns given by different crystals within a homogeneous sample frequently exhibit a wide range of variation, and each pattern must be interpreted separately in order to determine the symmetry elements common to all the patterns observed. A systematic approach to the analysis of crystal structure by means of single-crystal ED data would therefore necessitate the employment of statistical methods of synthesizing data obtained from a sufficiently large number of single-crystal patterns.

Morphology Examination Methods

The ordinary light microscope is undoubtedly still an indispensable tool in the examination of microcrystalline mixtures and hydrated paste structures. However, whereas it can be used to advantage for such purposes as the surveying of cement paste specimens, mineralogic and petrographic examinations of coarsely crystalline structures, and studies of residual unhydrated constituents of the course and rate of hydration, and of the distribution of larger pores and voids in cement paste, it is clearly incapable of revealing the finer details of paste structures, owing to the limited resolving power of visible light. According to Lea [10], "in a powdered set cement calcium hydroxide crystals can be detected and, occasionally, calcium sulphoaluminate, but the remainder cannot be differentiated". To provide a representative example of the information obtainable in microscope examinations of cement hydration, Lea can further be quoted on some interesting observations made by Brownmiller [11], "who noted that many of the cement particles were composite and that hydration proceeded by a gradual penetration into the particle from the surface. Except at, or near, the surface, therefore, the hydration of the coarser particles may not be very selective even though the hydration rates of the various cement compounds differ. Some of the interstitial material in the cement grains seemed to hydrate more slowly than the silicate crystals. A content of 10–15 percent of $Ca(OH)_2$ crystals was observed after 28 days".

The use of electron microscopy in cement hydration studies dates back about 20 yr, but it seems that different constructions of electron microscopes have only during the last decade reached such a high degree of reliability and versatility that they can be used for analytical work of a more systematic character. It has also been necessary to develop special methods of sample preparation and EM analysis, in order to avoid contaminations and artifacts, and, in the case of hardened pastes, to leave the original microstructure intact and undisturbed by various treatments.

The particle aggregates in hydrated cement materials are mostly so large and dense that the electron beam is completely absorbed in them, only the edge structures being observable. In order to facilitate the EM examination of cement-water reaction products, many investigators have selected to study the looser and more well-dispersed structures obtained in mixes containing a large excess of water, as compared with the w/c ratio normally used in pastes, and have thereby tacitly assumed that as long as saturation is maintained in the solution phase, the constitution and morphologic properties of the solid hydration product formed cannot differ very much from those of products formed in a paste. However, whereas the examination of more-or-less dilute suspensions can give a great deal of information on the microstructural properties of cement hydration constituents in their most well-developed states, the assumption of equality of phases is obviously, judging from various observations, justified only to a rather limited extent. The application of results obtained by using methods of preparation involving high water-to-solids ratios for drawing conclusions on the microstructure of setting and hardening pastes has also been criticized in the literature [1, 12, 13].

A method of letting extremely thin layers of cement paste of normal w/c ratios hydrate directly on the specimen screens for various times before introducing the specimen into the electron microscope has been devised by Bernard [14], and also adopted by Stork and Bystricky [15]. It is preferentially the contour structures in pore surfaces, and at the edges of cracks, that can be examined by this method, whereas the internal texture of aggregates of the colloidal particles is largely hidden from inspection.

For obvious reasons, it is necessary to break down hardened paste into a finely subdivided powder before it can be examined by EM methods. Clearly, any procedure used is likely to cause disturbances of the original paste structure in the form of fractures of crystalline materials, distortion of delicately built particles, etc. However, in the experience of some investigators, including the present author, ordinary methods of grinding and milling apparently leave most of the microstructural details relatively unaffected. The dry powder can simply be dusted on to the specimen support film, preferably by placing this film in the dust cloud formed in an elutriation column, or alternatively, it can be spread out in a thin and evenly distributed layer by means of electrostatic methods [16]. In order to improve the dispersion of EM specimens, the powder can also be suspended in a suitable organic liquid, and a drop of the suspension spread over the specimen support screen. Care must be taken, however, to make certain that the suspension medium does not produce any undesirable effects of interaction with the suspended solid particles. Ordinary laboratory ethyl alcohol has been found suitable in this respect, and also affords an excellent protection against carbon dioxide attack.

The application of more powerful techniques for achieving a high degree of dispersion of paste specimens, such as prolonged ball-milling or high-power ultrasonoration, will almost inevitably lead to serious disturbances, and eventually to complete disintegration of hydrated structures.

A technique involving replication of fresh cleavage surfaces of cement paste by evaporation of a thin film of highly resistant, and chemically inert, amorphous material, such as carbon, on to the surface, has been used by some investigators in later years. This method is supposed to give a true reproduction of the internal structures of the paste, and is likely to cause very little damage to the structure. Dehydration phenomena such as crumbling and cracking of the fractured paste surface may occur, owing to the unavoidable exposure of the paste specimen to the high vacuum necessary for a successful evaporation of the replica material. Difficulties in interpreting various observations must largely be overcome by comparing the replica structures with those observed in dispersed specimens using ordinary EM methods.

Microstructures of Lime Hydrate Modifications

Immediately upon mixing cement with water, Ca ions are dissolved from the surfaces of the calcium silicate crystals, and other Ca ions come from the dissolution of gypsum admixtures. In the highly supersaturated lime solution thus formed, CH crystals are precipitated out at an early stage of cement hydration. The XD diagram from portland cement paste also contains a strong and easily recognizable CH pattern, developed already in the first few hours after mixing, whereas patterns originating from other hydrated constituents are mostly weak and can be identified with certainty only by means of special methods [17]. As stated previously, CH is also the only crystalline hydrate readily detectable in the microscope, a content of 10 to 15 percent of CH crystals being observed after 28 days of paste hydration. A few percent more may be detected in fully hydrated paste, depending on the clinker mineral composition.

Macrocrystalline CH takes the form of hexagonal plates or prisms, and it is therefore rather surprising to find that in all the earlier studies of precipitates from lime solutions, whether formed by precipitation from pure solutions or by the decomposition of cement constituents, solid CH was identified as having the appearance of rounded platelets or spherulites which were found to grow into each other at the points of contact, forming long chains [18, 19, 20, 21, 22, 23, 24] (fig. 1).

The amorphous character of these formations is revealed by ED diagrams which show only a strong but very diffuse reflection at about 2.8 to 3.0 A.

The reason why CH precipitates in amorphous structures rather than in its natural crystalline habit was not given by the various observers. It was probably believed that in highly supersaturated lime solutions formed by rapid evaporation of water or in the first stages of cement hydration involving rapid dissolution of lime, especially from C_3S, a high concentration of small nuclei of CH crystals was momentarily attained, and that this unstable colloidal solution coagulated into spherulitic aggregates of an amorphous, frozen-in structure.

A simple, and apparently correct, description of the true nature of the spherulites, at least those formed from pure lime solutions, was given rather recently by Schimmel [25]. He observed that when spherulitic lime aggregates were moderately heated in the electron beam, they suddenly changed appearance, and simultaneously the easily recognizable pattern of calcite, $C\overline{C}$, appeared in the ED diagrams. Further heating in a beam of strong intensity caused the $C\overline{C}$ pattern to disappear gradually, being replaced by a ring pattern of calcium oxide, C, of cubic symmetry. Similar observations were reported earlier by Eitel [19], but were obviously overlooked by later observers, or considered to be of an occasional nature.

If rigorous precautions are taken to avoid carbon dioxide contamination, the precipitates forming in a supersaturated lime solution are observed to consist of well-crystallized particles, predominantly plates or slabs of a more or less regular, hexagonal shape.

These observations which have been confirmed by the present author, show that atmospheric carbon dioxide readily taken up by lime solutions may act as an inhibitor of the formation of the CH crystal lattice of regular hexagonal symmetry. Ordinarily, the microstructure of the $\overline{C}$-contaminated precipitates is that of chains of rounded platelets, but other formations of a similar nature and behavior have also been observed, such as networks of fibrous particles, or thin slabs with two parallel edges, exhibiting internal striations or cracks parallel to these edges [26]. These latter formations are obviously very easily decomposed in the electron microscope, the ED diagrams showing modified single-crystal spot patterns from oriented aggregates of calcium oxide.

Similar phenomena have been observed by Andrievskii, Tikhonov Shepinova, and Nabitovich [27], who also described the hardening process of lime mortar as being caused by bond formation in the superposition of growing hexagonal-plate crystals. These authors also explain the effect of sulfate in the mixing water as an increase in the rate of hydration and formation of the hexagonal-plate phase, combined with an inhibition of carbon dioxide attack. On the other hand, the introduction of a small amount of a surface-active agent, sulfite alcohol waste, with the mixing water is observed to prevent the growth of larger crystals, and the hardening mass remains for some time in a state of very fine subdivision.

In specimens containing lime solutions which have been exposed to the attack of atmospheric carbon dioxide for a longer time, $C\overline{C}$ has been observed to take the form of regular crystals of calcite, mostly appearing as rhombic slabs, with the crystalline angles of calcite, superimposed in aggregates with sawtooth-shaped edges [20, 21, 22, 23].

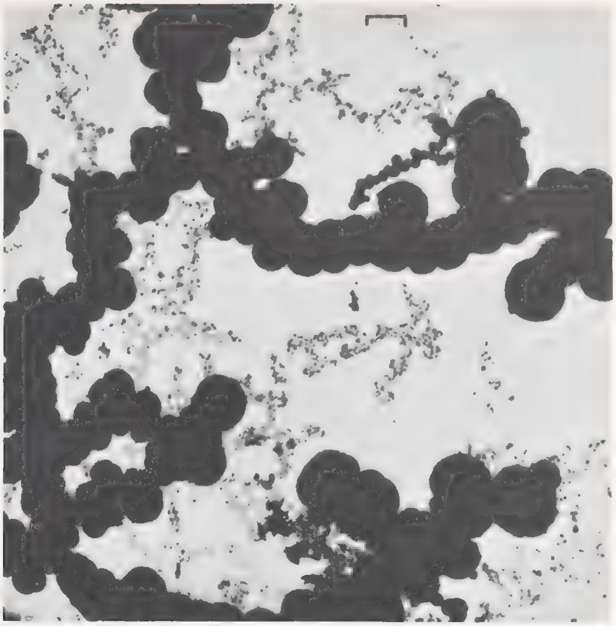


FIGURE 1. *Calcium hydroxide chains precipitated from solution in the presence of carbon dioxide contamination.*

It can be expected that the process of regular crystallization of CH will be disturbed by the presence in the lime solution even of certain ionic groups other than $\overline{C}$ anion. Brunauer, Kantro, and Copeland [28], in studying the stoichiometry of C_3S and β-C_2S hydration products, found that certain quantities of CH which, for stoichiometric reasons, were expected to be precipitated in the samples, could not be accounted for by the data obtained in XD quantitative mineral analyses. The most probable explanation for the apparent absence of this quantity of lime was found to be that a minor part of the amount of solid CH resulting from the hydrolysis of the anhydrous silicates was present in an amorphous, or at least very poorly crystallized, state, owing to lattice disturbances caused by inclusions of silica groups. Electron-microscopical observations on paste-hydrated materials from these studies confirmed the presence of considerable quantities of more or less amorphous-looking matter, part of which could well be imagined to be composed of disordered aggretates of extremely small CH crystal nuclei.

The normal appearance of CH crystallized in cement pastes and in suspensions protected from the attack of carbon dioxide is that of plates. These are sometimes of comparatively large dimensions, more than 1 μ across, but mostly so thin that they are transparent to electrons.

Examples of electron micrographs and ED patterns of CH plates in cement pastes and similar preparations have been given in various reports [29, 30, 31, 32, 33, 34]. One such plate is shown in figure 2 a, b. The identification of CH crystals is readily made by means of their characteristic and mostly well-developed ED patterns which, due to the effect of orientation, contain in general only the hexagonal (hk.0) (prism) reflections corresponding to the unit cell $a_H=3.59$ A.

In cement slurries of higher w/c ratios than is normal in paste hydration, numerous CH crystals, of comparatively small dimensions and mostly very thin, are observed to precipitate out at an early stage of reaction. Owing to conditions of crystallization which are less cramped than in ordinary paste hydration, these CH plates often assume the habit of almost regular hexagons. An example is given in figure 3 a, b, where some plates are observed to stand more or less on edge, resulting in the appearance in the ED diagram of reflections from oblique (hk.1) lattice planes. In other diagrams even the basal (0001) reflection at 4.91A lattice planes is occasionally observed.

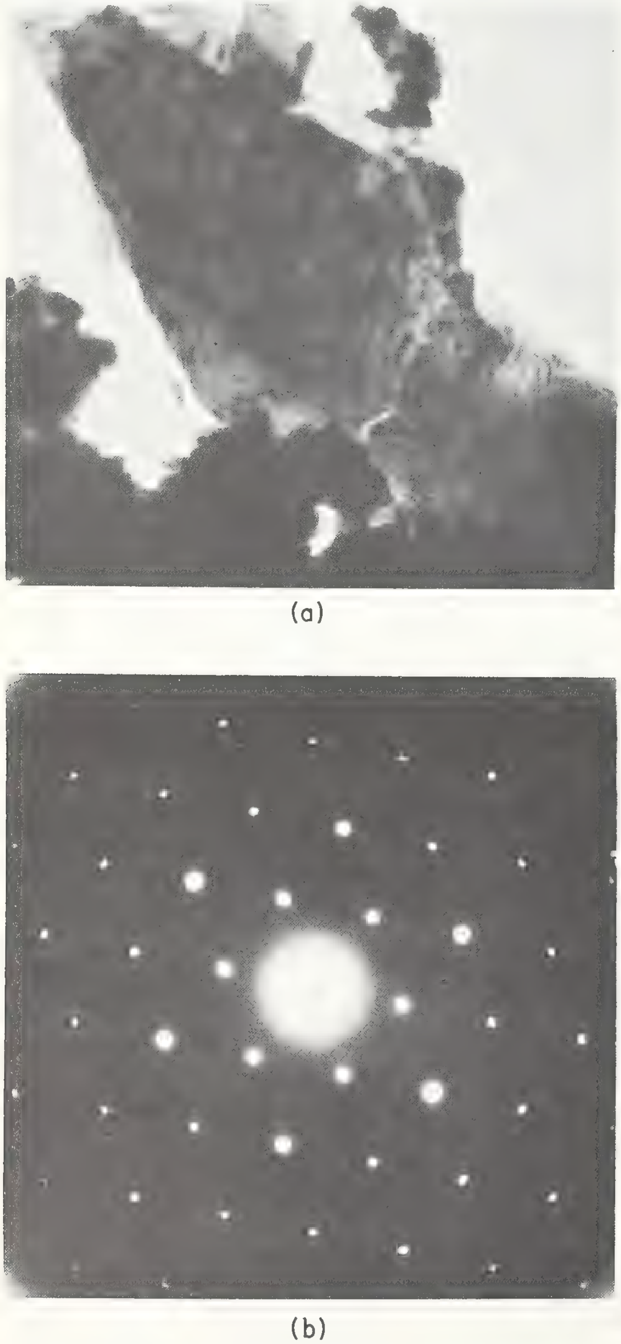


Figure 2. *(a) Calcium hydroxide plate as formed in cement pastes and similar preparations. (b) Electron diffraction pattern of calcium hydroxide plate shown in figure 2a.*

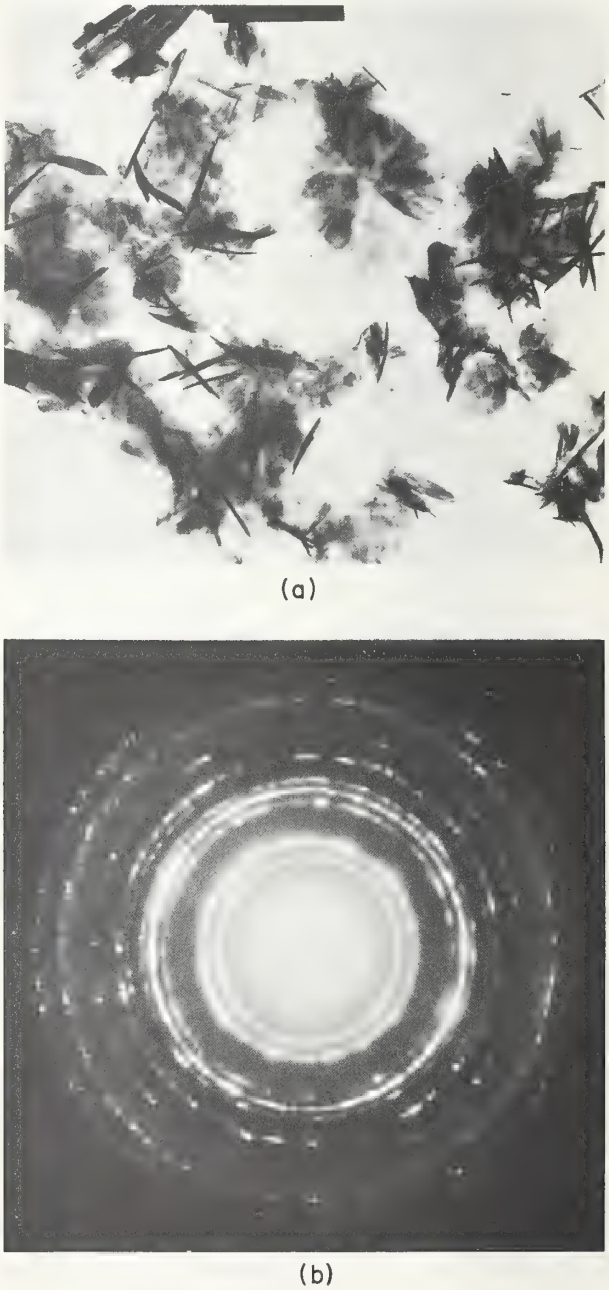


Figure 3. *(a) Calcium hydroxide plates formed in a cement slurry of high w/c ratio. (b) Electron diffraction pattern of calcium hydroxide plate shown in figure 3a.*

General Character of Compounds in the C–A–F–H System, and of Complex Salts

The subject indicated by the heading has been treated in detail in another review article at the Symposium, and will be reviewed here only in very broad outline.

The only compound stable in the low-temperature region of the system C–A–H, except AH_3 and CH, seems to be the hydrate end member of the hydrogarnet series, C_3AH_6 [35]. The characteristic isometric crystal shapes of this compound well known from a number of microscope observations, have also been observed in EM studies to form in large amounts in e.g. rapidly mixed suspensions of pure C_3A in water, and with crystal sizes of the order of 1 μ [26].

Metastable hexagonal-plate phases are very frequently observed to be the products first formed in the hydration of the aluminate components of cement, and to persist over long periods. The crystalline compounds which are of greatest interest in connection with cement hydration, are generally assumed to have the composition C_4AH_{13} or C_4AH_{19}, depending on the state of hydration, and C_2AH_8, together with forms intermediate between these, of the character of mixed-layer compounds. Analogous compounds are formed in the C–F–H system, and in the C–A–F–H system various types of solid-solution compounds are possible. The stability of the hexagonal phases seems to increase with the content of F, and it is even reported that a stable C_3FH_6 hydrogarnet compound does not exist [36].

The hexagonal-plate phases have been observed in several optical and EM studies on products of hydration of C_3A and $C_2(A, F)$. A typical electron micrograph and ED pattern combination is shown by Buttler, Dent Glasser, and Taylor [37]. The ED patterns of the pure compounds are strictly hexagonal, giving a unit cell of about $a_H=5.7$ A. Isomorphous substitutions of different cations for protons, e.g., $\overline{C}$ for 2 H in the natural mineral hydrocalumite, lead to deviations from exactly hexagonal symmetry. The first transformation occurring upon heating consists in the formation of oriented layers, of the CH type and unit cell (about 3.6 A), within the matrix of the original structure. The common occurrence of this type of transformation, as described by Buttler, Dent Glasser, and Taylor, has been observed also by the present author. Thus, upon heating in unsaturated conditions to temperatures of 100° C or somewhat higher, the hexagonal phases seem to convert more easily to another hexagonal layer lattice hydrate phase than to the isometric hydrogarnet structure, supposedly stable in this temperature range.

In reconsidering the crystal structure originally suggested [38], Buttler, Dent Glasser, and Taylor proposed a model for $C_4A{\cdot}aq.$ consisting essentially of an octahedral layer of the type occurring in CH however with Ca ions in ⅓ of the octahedral positions replaced by Al ions and with hydroxyl and water groups accommodated outside this layer. The Al ions are arranged in an ordered pattern with a unit cell a_H of about 5.7 A, a distance intermediate between the orthohexagonal cell distances of CH and AH_3 (gibbsite) which are about 6.2 and 5.0 A, respectively.

The compound $C_4A{\cdot}aq.$ has a number of comparatively well defined states of hydration, judging from the dehydration curves of Buttler, Dent Glasser, and Taylor, and including the most saturated state C_4AH_{19}, according to Jones and Roberts (ref. [7] of review paper by Jones, this Symposium). The sequence of layers within the molecular units is illustrated diagrammatically at the foot of the page, with the contents of each layer given per orthohexagonal unit cell ($a_H \times a_H\sqrt{3}$).

As suggested by Jones, the $C_2A{\cdot}aq.$ structure can be derived from that of C_4AH_{19} by substituting Al ions for protons in the intermediate double layer of water, according to the following model.

	——2 Al——
	3 H_2O+4 OH
	6 OH
2 C_2AH_8 c_o=10.7 A	4 Ca+2 Al
	6 OH
	3 H_2O+4 OH
	——2 Al——

An alternative principle of arrangement of these structures presents itself on noting the great sim-

C_4AH_{19} $\longrightarrow$	C_4AH_{13} $\longrightarrow$	C_4AH_{11} $\longrightarrow$	C_4AH_7
c_o=10.7 A	8.2 A	7.9 A	5.8 to 6.5 A
6 H_2O+OH——	6 H_2O+2OH——	4 H_2O+2OH——	2OH——
6 OH	6 OH	6 OH	6 OH
4 Ca+2 Al	4 Ca + 2 Al	4 Ca+2 Al	4 Ca+2 Al
6 OH	6 OH	6 OH	6 OH
6 H_2O+OH ——	6 H_2O+2OH ——	4 H_2O+2OH——	2OH——

ilarity of the C–A–F–H phases to clay minerals. As is well known, the molecular unit layers of clay minerals consist of $(M(6)O_2)_n$ layers, with M(6) denoting cations in octahedral positions (in clays usually Al or Mg ions), unilaterally or bilaterally polymerized with $(M(4)_2O_5)_n$ layers, with M(4) denoting cations in tetrahedral positions (in clays usually Si ions). Separate $(M(6)O_2)_n$ layers occur in some types of clay minerals. Excessive negative charge is balanced by introducing a suitable number of protons. In the isolated state, the layer units possess hexagonal symmetry, but polymerization and stacking lead to lower crystal symmetry, monoclinic or triclinic.

It is generally assumed that octahedral CH (or $(CaO_2)_n$) layers and tetrahedral S_2H (or $(Si_2O_5)_n$) layers cannot polymerize, because of a too-large misfit of the hexagonal unit cell sizes. This is considered to be the reason why no C–S–H minerals of the clay-type structure have been found. On the other hand, Al ions can occur in tetrahedral AlO_4 coordination, and a hypothetical $(Al_2O_5)_n$ layer would have a calculated cell size a_H of about 6.2 A, approximately equal to the orthohexagonal cell size in the CH layer.

Such a unit, with all the tetrahedral sites filled, would probably be highly unstable, but it is conceivable that partly filled $(Al_{2q}O_5)_n$ layers can combine with partly filled $(Ca_pO_2)_n$ layers (q and p denoting degrees of filling) to form a structural element in which the two components stabilize each other, and in which the positive charge deficiency is compensated for by protons. The C_4A·aq. and C_2A·aq. structures originally suggested by Tilley, Megaw, and Hey [38] are essentially of the type now described. It seems natural to modify these proposed structures in such a way that the structure models related to C_4A·aq. would be isomorphs of the 1:1 kaolinite-type clay structure, those related to C_2A·aq. isomorphs of the 2:1 montmorillonite-type clay structure.

It can be further noted that extra water molecules can be accommodated in the "holes" of $(M_2O_5)_n$ layers, one molecule per hexagonal unit cell and sheet, without any essential increase of the basal spacing. The formation of CH-type layers upon dehydration can be interpreted as a collapse of the tetrahedral layers, the Al ions being accommodated in the empty octahedral positions, or segregating in the form of amorphous alumina hydrate.

In similarity to clays, mixed-layer compounds may form, with layer sequences of, e.g., C_4A·aq.-C_2A·aq.-C_4A·aq., etc., possibly accounting for the observations of formation of C_3A·aq. reported in the literature.

Possible layer sequences for various C–A–H compounds are indicated in the following diagrams, in which the compatibility with known data for the composition and cell sizes have been taken into consideration. Partial or complete replacement of Al ions by Fe ions can occur, but is not indicated.

C_4AH_{19}	→	C_4AH_{13}	→	C_4AH_{11}	→	C_4AH_7
——6 H_2O——		———		———		———
6 OH+2 H_2O		6 OH+2 H_2O		6 OH		6 OH
2 Al		2 Al		2 Al		3 Ca+2 Al
2 OH+4 H_2O		2 OH+4 H_2O		2 OH+4 H_2O		6 OH
4 Ca		4 Ca		4 Ca		———
6 OH		6 OH		6 OH		+
——6 H_2O——		———		———		———
						OH
						Ca
						OH

C_2AH_{9-7} c_o=10.7 to 10.4 A (Roberts [100])	$C_3A_3H_{28}$ ("CAH_{10}") c_o=14.3 to 14.6 A
———	———
6 OH(+2 H_2O)	6 OH+2 H_2O
2 Al	2 Al
4 OH+2 H_2O	3 OH+3 H_2O
4 Ca	3 Ca
4 OH+2 H_2O	3 OH+3 H_2O
2 Al	2 Al
6 OH(+2 H_2O)	6 OH+2 H_2O
———	———
	3 OH+3 H_2O
	2 Al
	3 OH+3 H_2O
	———

Under the conditions prevailing in the reaction of portland cement with water, the formation of hydrated C—A—F—H compounds is likely to be influenced by the presence of varying amounts of admixtures, specifically sulfate ions from gypsum, which are incorporated in the C—A—F—H compound structures, forming complex salts of widely varying types and compositions [36, 39, 40].

It is generally postulated that two series of such complex salts exist, the generalized oxide formulas of which are usually written $C_3A \cdot CY \cdot H_m$ and $C_3A \cdot (CY)_3 \cdot H_n$, with Y denoting a structurally equivalent unit amount of a large number of oxides. For the cement hydration system, substitutions of H, $\overline{S}$, $\overline{C}$, and even S for Y are of greatest interest.

The clay-type structure model containing voids in tetrahedral and octahedral cation positions can be applied in conceiving hypothetical crystal structures even for these compounds. Some examples are given below.

It can be added that the hexagonal unit cells of all the compounds for which structure diagrams have been given above have been observed to be either in the vicinity of $a_H = 5.7$ A, or simply related to this distance ($a_H\sqrt{3}$, $2a_H$) in the case of compounds with larger true unit cells. A possible exception is the "gehlenite hydrate", for which Fratini and Turriziani [102] give a hexagonal unit cell of 8.85 A. However, the cell size 9.96 A ($5.75\sqrt{3}$) given recently for this compound by Schmitt (see discussion of paper by Jones, this Symposium) seems to be based on more reliable XD data. A similar hexagonal cell unit, 8.8 A, was found for $C_4A \cdot aq.$ and $C_2A \cdot aq.$ in an earlier work by Wells, Clarke, and McMurdie [103], but more recent studies have given values related to 5.7 A [37].

In the diagram for "gehlenite hydrate" below, two alternatives are given, of which the latter one represents an attempt to explain the comparatively large spacing of 12.4 to 12.7 A, as found by different observers. This model contains Si—OH apices of tetrahedra directed outwards from the molecular layer, and is thus a hypothetical analog of the much-debated Edelman-Favejee model for the structure of certain clay minerals [104].

The structure indicated for ettringite is an alternative to the zeolitic structure suggested by Bannister [41], the details of which have not been confirmed by a complete structure analysis. Obviously, further work is needed for the establishment of the details of this structure, as well as of all the structures in the group of compounds now described.

Isomorphous substitution of Fe ions for Al ions leads in general to a somewhat larger unit cell, due to the slightly larger equivalent ionic radius of the Fe ion. In the case of phases in the hydro-

$C_4A\overline{S}H_{16}$(?)	→	$C_4A\overline{S}H_{14}$	→	$C_4A\overline{S}H_{12}$	→	$C_4A\overline{S}H_{10(\rightarrow 8)}$(?)
"low sulfate sulfoaluminate" [100, 101]						
$c_o = 10.4$ A	→	9.5 A	→	8.9 to 9.0 A	→	8.2 A→8.0 A.
——6 H_2O——		——4 H_2O——		——2 H_2O——		————
6 OH+2 H_2O		6 OH+2 H_2O		6 OH+2 H_2O		6 OH (+2 H_2O)
2 Al+S_2		2 Al+S		2 Al+S		2 Al+S
2 O+4 OH		2 O+4 OH		2 O+4 OH		2 O+4 OH
4 Ca		4 Ca		4 Ca		4 Ca
6 OH		6 OH		6 OH		6 OH
——6 H_2O——		——4 H_2O——		——2 H_2O——		————

C_2ASH_7		C_2ASH_8	$C_6A\overline{S}_3H_{30-34}$	
"gehlenite hydrate"			ettringite	
$c_o = 12.4$ to 12.7 A			$c_o = 10.8$ A (41)	$C_4A\overline{C}H_{11}$ *
		————		hydrocalumite
	or	OH		$c_o = 7.86$ A
————		Si	——6 H_2O——	————
6 OH+2 H_2O		6 OH+2 H_2O	6 OH(+2 H_2O)	6 OH+2 H_2O
2 Al+Si		2 Al	Al+1.5 S	2 Al+C
2 O+4 OH		O+5 OH	6 OH	6 OH
4 Ca		4 Ca	3 Ca	4 Ca
2 O+4 OH		O+5 OH	6 OH	6 OH
2 Al+Si		2 Al	——6 H_2O——	————
6 OH+2 H_2O		6 OH+2 H_2O		
————		Si		
		OH		
		————		

---

* The hydrocalumite studied by Buttler, Dent Glasser, and Taylor held much less $\overline{C}$, approximate formula unit $C_4A\overline{C}_{\frac{1}{2}}H_{12}$.

garnet series, $C_3(A,F)(S,H_2)_3$, it has been suggested by Jones that the expanding and labilizing effect of the introduction of increasing amounts of Fe ions into the lattice is counteracted by the simultaneous uptake of Si ions in tetrahedral sites, the SiO_4 group requiring less space than the $(OH)_4$ tetrahedral group. It is probable that similar substitutions influence also the formation of phases within the hexagonal structure group under various conditions when silicon ions are present, as for example in a cement-water mixture. The sulfur and carbon ions, with six and four positive charges, respectively, have very small equivalent ionic radii and are easily accommodated in oxygen tetrahedra. They can therefore be expected to have a similar, stabilizing effect on the formation of the C–A–F–H solid-solution phases.

The size of the hexagonal unit cells may obviously be influenced also by the degree of occupation of octahedral cation positions. According to available data, most of the compounds now discussed possess hexagonal, or pseudohexagonal, unit cells relatable to a distance between 5.6 and 5.8 A. The exceptions are CAH_{10} (5.46 A) and ettringite (5.55 A). It is perhaps significant that in the hypothetical structures indicated above, the octahedral sites are only half-filled in these compounds, but two-thirds filled in all the others.

C—A—H and Related Phases in Hardened Portland Cement Paste

Of C–A–F–$\bar{S}$–H compounds possibly present in hardened pastes, only the hexagonal-plate phase has been observed by the author [26, 32, 33, 34]. In crushed or ground paste samples the hexagonal shape is of course less evident than in the C–A–H plates formed in suspensions. Figure 4 a, b shows the characteristic appearance of such a plate from a nearly 10-yr-old paste sample, together with amorphous-looking or fibrous C–S–H material. The ED single-crystal pattern corresponds to a nearly hexagonal unit cell, $a_H=5.70$ to 5.62 A, as measured in different directions of the pattern with strong spots. Weaker spots halfway between the stronger ones indicate that the true unit-cell length is twice that given above, and prove the existence of a superstructure in this crystal, as well as in the majority of crystal plates of this type found in pastes. This doubling of the 5.7-A unit cell seems in most cases to be connected with deviations from exact hexagonal symmetry, whereas in ED patterns from hexagonal-plate crystals obtained by the hydration of C_3A, in water or in lime solutions, superstructure spots and measurable deviations from perfect hexagonal symmetry cannot be detected. These facts are indicative of a lattice with isomorphous ionic substitutions of F or $\bar{S}$ for A, or alternatively, with $\bar{S}$ replacing void tetrahedral groups. The composition can probably be approximated by the formula $C_4(A,F,\bar{S})\bar{S}H_{10}$. The substitutions are believed to be of the ordered type, but the evidence is inconclusive on this point.

Plate crystals of the C–A–H type occur in small quantities in nearly all paste samples examined, but the ED patterns are not always as easily interpreted as in the example now given. The superstructure spots may be very weak, the pattern of strong spots may have an irregular intensity distribution, and the reflections may be

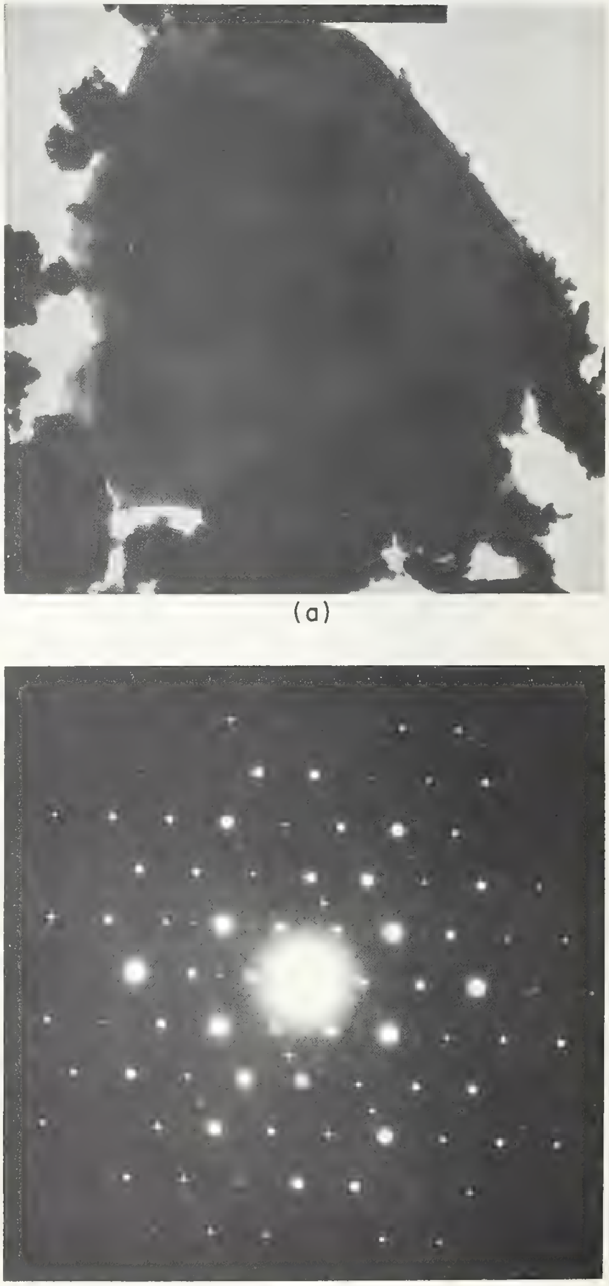


FIGURE 4. *(a) Calcium aluminate hydrate plate from a 10-yr-old hardened paste. (b) Electron diffraction pattern of calcium aluminate hydrate plate shown in figure 4a.*

Weak spots indicating a true unit-cell length of 11.24 to 11.40 A are shown.

diffuse or streaky. All these effects indicate the presence of various types of disorder in the corresponding lattices.

A commonly observed phenomenon is that the C–S–H gel particles tend to develop fibrous structures in the vicinity of the C–A–H plates, and that fibers of tobermorite are adsorbed on their surfaces. An extreme case is shown in figure 5 a, b, taken from a highly porous paste. The spot pattern, corresponding to $a_H = 2 \times 5.70$ A, is superimposed by a spot-ring diagram from the CSH(B) tobermorite fibers. The implication of this observation would be that the hexagonal C–A–H phases take an active part in the formation of paste structures, first, by acting as a kind of template for other structures crystallizing in the vicinity of its surfaces, and second, by forming bridges between gel structures adhering to different parts of the plate surfaces.

On the other hand, the plates are rarely observed to form coherent structures linked together by the coalescence of partially overlapping plates. A similar mechanism is regarded by Rehbinder [42] and his associates to be responsible for the process of setting of cement pastes of the quick-setting type, i.e., without gypsum or surface-active-agent admixtures. However, in normal portland cement pastes, the structures causing the initial set are probably of a different type, due to the formation of sulfoaluminate hydrate and so-called adsorptive modifications of hydroaluminate caused by surface-active agents [43]. The C–A–H crystal plates in old pastes may be secondary formations, resulting from a process of recrystallization following the breakdown of structures developed during the period of setting.

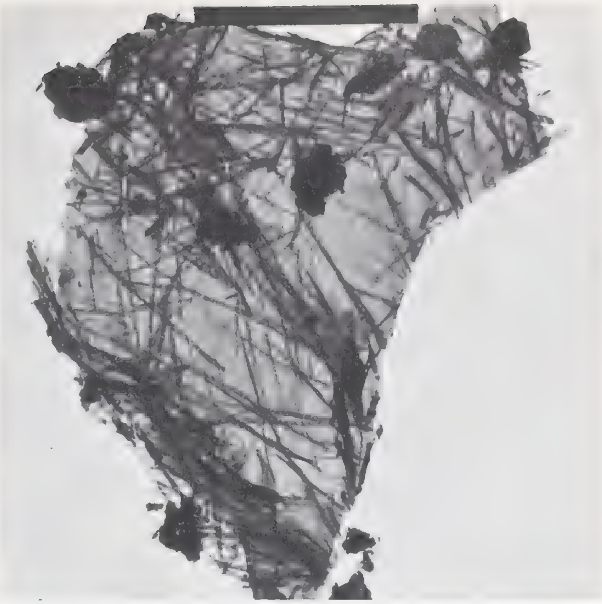
Judging from the common occurrence of particles of the hexagonal C–A–H phase even in old pastes, the expected transformation to the isometric $C_3(A,F)H_6$ compound does not take place. As mentioned previously, the isomorphous replacements and possibly the introduction of additional cation complexes seem to stabilize the hexagonal structure.

Ettringite and Related Phases

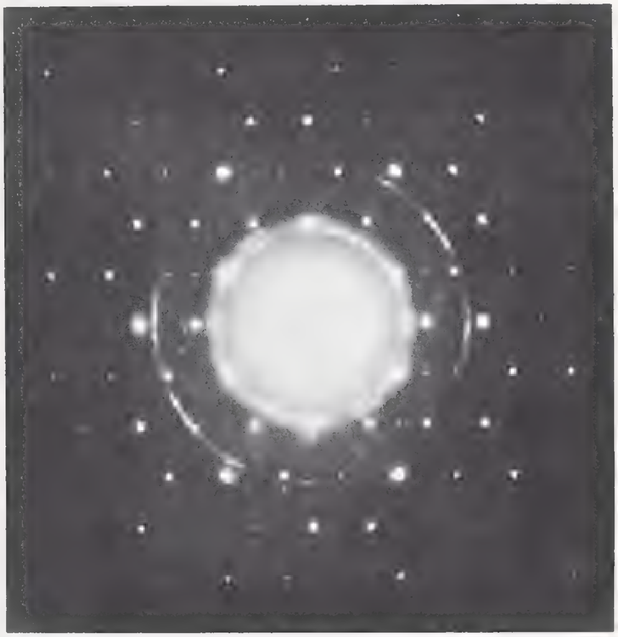
The characteristic crystal habit of ettringite, as reported from microscopic examinations, is that of long rods or needles or, in well-crystallized specimens, that of hexagonal prisms with sharply cut off end faces. EM studies by Iwai and Watanabe [44] show this compound in the form of heavy rods or splines.

Particles of the described habit have not been observed in cement pastes examined by the present author. It is very unlikely that ettringite can be kept from decomposing in the electron microscope without taking special precautions of cooling the specimen. However, if present in a paste, it may be expected to form pseudomorphs upon rapid dehydration.

At the London Symposium, Nurse and Taylor [17] presented XD evidence for the presence of ettringite in a sample of old paste. Unpublished XD data for hardened cement paste, obtained by the author, also showed a number of reflections considered to be characteristic of ettringite. The intensities of the ettringite reflections were about



(a)



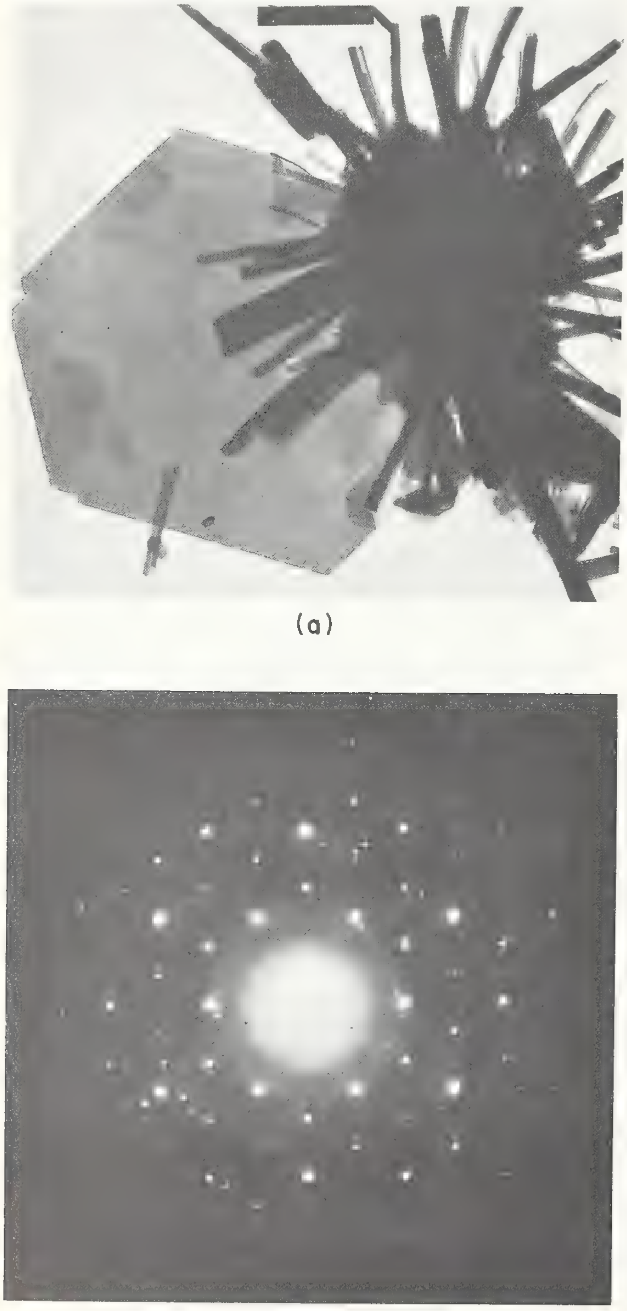
(b)

FIGURE 5. *(a) Tobermorite fibers, CSH(B), formed in vicinity of calcium aluminate hydrate plates in a highly porous paste. (b) Electron diffraction pattern of material shown in figure 5a.*

w/c=1.5.

The spot pattern corresponding to $a_H = 2x5.70$ A is superimposed by a spot ring pattern from the tobermorite fibers.

equally strong from 2 days to 1 yr of age of the paste samples. On the other hand, Taylor [45] observed, in another series of paste samples, that the ettringite reflections disappeared after a couple of weeks, and were replaced by reflections belonging to a compound isomorphous with C_4AH_{13}. Other workers have reported the decomposition of ettringite upon storing in air or upon heating at 40 to 80 °C, yielding gel-like products. A detailed account of XD data obtained recently on the appearance of ettringite and other sulfoaluminate phases in cement pastes is given by Copeland and Kantro (this Symposium).


(a)

(b)

Figure 6. (*a*) *Hydration products formed by 24-hr shaking of a slurry of Type I portland cement.* (*b*) *Electron diffraction pattern of material shown in figure 6a.*

w/c=4.

A hexagonal plate of C_4AH_{13} is shown together with a cement covered with splines pseudomorphic possibly of a $C\text{–}A\text{–}\overline{S}\text{–}H$ compound.

It may be of interest in this connection to describe some observations made by the present author [26, 34] of the hydration products of a Type I portland cement after 24 hr of shaking in a slurry with w/c=4. The character of the slurry constituents is shown in figure 6 a, b. Disregarding the hexagonal plate of C_4AH_{13} structure which gives the ED spot pattern of figure 6b (corresponding to a hexagonal cell $a_H=5.68$ A), it is seen that the original cement grains are covered with thick, radiating splines or rods, of a habit associated with ettringite. It is likely that these formations are only pseudomorphs of an easily dehydrated structure originally present, since the ED patterns contain no trace of crystalline diffractions, except sometimes a very diffuse ring at about 2.7 to 3.2 A. Judging from the abundance of these structures, in comparison with the normal content of $\overline{S}$, amounting to about 2 to 3 percent, in commercial portland cements, and taking into account the fact that the splines appear to form from the material in the surface of the C–S anhydride particles, it seems unlikely that silica groups do not take part in building up these structures. It is very tentatively suggested that they are composed of a $C\text{–}A\text{–}S\text{–}\overline{S}\text{–}H$ compound of the ettringite variety, $C_6(A,F)(S,\overline{S})_3H_n$, in which, upon the structural collapse following dehydration, a fibrous internal structure is still retained, due to the formation of polymerized silica chain elements.

However, even various forms of pure calcium sulfoaluminate hydrates can be partly deprived of their water of crystallization, without apparent change in outer form, as shown by EM data given by Astreeva and Lopatnikova [46].

After a few days of standing in paste form, the rod-like elements became covered with a felt-like mass of crinkly foils of CSH(B) tobermorite developing from the surfaces of the cement grains, and simultaneously the rod elements seemed to loosen up and unfold (fig. 7). This change may indicate that some structural elements are being replaced by others, e.g., A and $\overline{S}$ by S, leading to structural rearrangements.

It is evident that the suggestions now made are of a very uncertain nature, and there are probably alternative ways of interpreting the phenomena observed. However, it seems worthwhile to include these observations here, in order to indicate an important problem for future research. It may well turn out that the effect of admixtures of sulfate and similar ions on structure formation is more complicated than is generally assumed.

Although a coherent picture of these processes has yet to be attained, at least some of the available data seem to indicate that the first stages of structure development in setting cement paste are

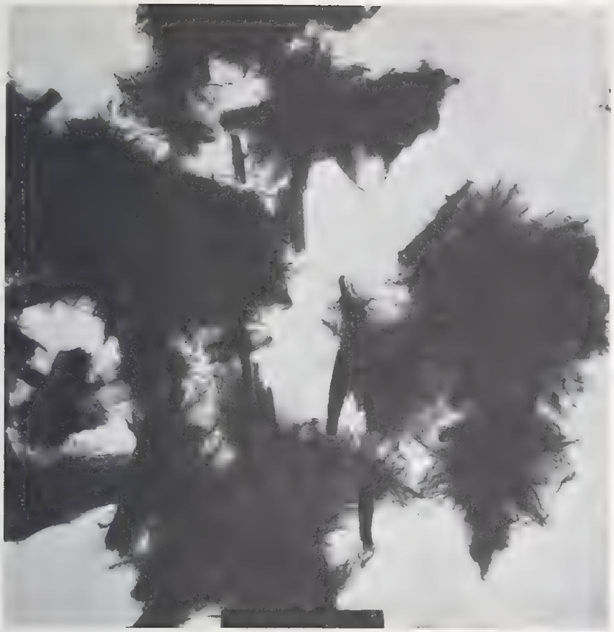


FIGURE 7. *Tobermorite, CSH(B), foils formed in a cement slurry on standing.*

governed by a delicate balance in the composition of the minor anhydrous phases and admixtures, and by the formation of complex C–A–F–S–$\bar{S}$–H phases which, although of a transient nature and later decomposing, still leave their imprint on the structures developing in the subsequent processes of hardening.

Structures similar to those described by the author as heavy splines, have been observed in cement hydration studies by Sliepcevich, Gildart, and Katz [20], by Smolnikov [22], who identified them as ettringite, and by Boutet [21], who observed them in such abundance that he considered them to be C–S–H compounds which, due to their densification and interlocking in fibrous networks, gave a major contribution to the development of strength in cement paste. The structures formed in C_3A suspensions with small admixtures of lignosulfonate [24, 42] may be of a related type.

The so-called "stressing cement" developed by Mikhailov [105] (cf. also his paper in this Symposium) represents an interesting application of the principles of crystal chemistry and microstructural development in the sulfate-cement field. This cement is a specially proportioned mixture of portland cement, high-alumina cement, and gypsum, and its reaction with water is characterized by the formation of a paste structure consisting of an expanding framework of high-sulfate sulfoaluminate crystals, and C–S–H gel material accommodated in the meshes of this framework. Under certain rigorously specified conditions of curing, this composite system of particles integrates and hardens to a mass of high strength. Similar principles of structure formation are employed in other types of expanding cements, such as the well-known Lossier cement, developed in France.

Microstructures of Calcium Silicate Hydrates

General Remarks

Schematic phase diagrams of the C–S–H system were presented at the London Symposium [8, 47]. Although a great number of studies of various compounds and phase relationships within the C–S–H system have since been executed, no major changes in the general outlines of these schematic diagrams have been introduced.

In the products of normal cement hydration, the phases occurring in the low-temperature region of the C–S–H phase diagram, viz. the CSH(B) and C_2SH_2 tobermorite phases, seem to predominate. However, some investigators have presented evidence for the appearance of other compounds, such as $C_3S_2H_3$ afwillite, $C_2SH(B)$ hillebrandite, and $C_2SH(A)$ in various preparations obtained in the hydration of portland cement or its pure silicate constituents. These and other compounds are also likely to be present in cement paste products autoclaved at elevated temperatures, and have in fact been identified and studied in various hydrated cement samples. For this reason, it seems worthwhile to review separately the most essential microstructural properties of various C–S–H materials.

Arrangements of Lattice Elements in C–S–H Structures

The formation of lattice structures from the structural elements of the C–S–H system, i.e., $Si(OH)_4$ tetrahedra, Ca ions, and O ions with or without attached protons, is commonly recognized to be governed by a few simple principles.

A factor of primary importance is the tendency of free silica groups to polymerize into larger complexes, such as rings, chains, layers, and networks [48, 49], each condensation of pairs of tetrahedra being accompanied by the expulsion of a water molecule. A second factor is that the Ca ion has a great capacity of accommodating itself in oxygen or hydroxyl coordination polyhedra of widely varying type and coordination number. A natural consequence of these circumstances is that the groups involved may combine into crystalline structures in a great number of different ways.

Further, the difference in lattice energies of two alternative compound compositions is often small, and the rate of transformation low, causing certain compounds which are in reality unstable under the prevailing thermodynamic conditions to persist over long periods without changing observably.

In a few C–S–H compounds, the silica constituent of the lattice is present in the form of unpolymerized, isolated SiO_4 tetrahedra. The two most well-known of these compounds are $C_3S_2H_3$ (afwillite) and $C_2SH(A)$, both containing discrete $SiO_3(OH)$ ions as lattice constituents. It is natural that such compounds are found among those having a comparatively high C/S ratio, where the tendency of polymerization of silica groups is counteracted by the presence of relatively large amounts of Ca, O, and OH ions that tend to screen the SiO_4 groups from each other.

The three-dimensional character of such lattices promotes the growth of crystals of macroscopic size, and this is perhaps the reason why of all C–S–H structures those of afwillite and $C_2SH(A)$ were the first ones to be determined [50, 51]. Another hydrate compound of similar type which has been described recently with respect to its crystallographic properties, is C_5S_2H, calcio-chondrodite [52], which has a structure closely related to that of γ-C_2S, with discrete SiO_4 groups. The high-lime end member of the C–S–H system, $C_3SH_{1.5}$, is believed to contain isolated Si_2O_7 groups as structural elements [53]. However, judging from the observed fibrous habit of $C_3SH_{1.5}$ particles, the presence of chains of silica would seem to be a more likely alternative.

The C–S–H compounds possessing a more or less clearly pronounced fibrous particle habit have attracted special attention because of the relationships probably existing between one or more of these phases and the fibrous constituents of cement paste. The repeat unit distance of about 7.3 A along the fibers has been observed to be common to all fibrous C–S–H compounds. The true nature of the structural elements causing this repeat unit to appear was first established in studies of the structure of the anhydrous mineral CS, wollastonite [54, 55, 56], for which the previously suggested structure containing Si_3O_9 rings was found to be essentially incorrect and was replaced by a structure containing metasilicate chains of ideal composition SH and a repeat unit of Si_3O_9 ($Si_3O_3(OH)_6$ if written formally as a silicic acid).

A characteristic feature of this 3-metasilicate chain is that on one side of the chain the free OH—OH tetrahedral edges perpendicular to the chain axis are spaced at intervals of about 3.65 A along the axis, whereas on the opposite side the repeat distance is 7.3 A. It can be observed that the minimum need of space across the chain is equivalent to the space occupied by an OH—OH group, or about 5.6 A.

In the wollastonite structure, the chains are arranged in layers of parallel-oriented separate chains, with Ca ions accommodated in the oxygen polyhedra formed by superimposed layers of chains. The various forms of wollastonite can be described as polymorphic modifications corresponding to different alternatives for the arrangement of 3-metasilicate chains in layers.

The simplest possible silica group formed by condensation of 3-metasilicate chains is of course the double chain, of composition Si_6O_{17}. Mamedov [57] showed that in the structure of xonotlite, of ideal composition C_6S_6H, layers of such double chains alternate with layers of Ca ions. Liebau [48] gives a list of minerals, among them several C–S–H compounds, in which the silica groups are likely to occur as such double 3-metasilicate chains.

The double chain in xonotlite contains 8-membered rings of SiO_4 tetrahedra. By further edge-to-edge condensation of Si_6O_{17} chains, in which process 5-membered rings of tetrahedra are formed, a polymerized sheet of composition Si_6O_{15} may be built up. It has been suggested by Mamedov and Belov [58] that such layers, stacked in various ways together with Ca and OH ions, occur as the structural elements common to a number of C–S–H minerals of low C/S ratio, the okenite-nekoite group with fibrous crystals [59], and the truscottite-gyrolite group with tabular crystals and hexagonal or trigonal symmetry [60, 61]. Although nothing is known with certainty about the details of these structures, it seems possible that in the first group the Si_6O_{15} sheets are stacked with the fiber axes of different sheets parallel-oriented, whereas in the second group more or less orderly trigonal rotations of the sheets take place in the process of superposition.

An alternative structure of the silica sheet, analogous to the $(Si_2O_5)_n$ sheet occurring in clay minerals, was considered in the analysis of gyrolite by Mackay and Taylor [61] but was rejected by them, since the distortion of the sheet necessary to fit it in the observed unit cell would be unduly large. It may be worth pointing out that just as in the case of the hexagonal C–A–H phases described in the previous section, it would be possible to obtain a fit with observed data on composition, unit cell, etc., by assuming the existence of tetrahedral and octahedral voids and proton substitutions in the structure of minerals of the truscottite-gyrolite group. However, some difficulties would be raised because of the relatively low content of water of crystallization of these minerals, leading to a low degree of proton substitution computed for hypothetical lattices of this type. Further, a conversion into chain structures (wollastonite), observed to occur upon heating, would seem unnatural, if no chain elements were present in the unheated minerals.

None of these compounds is likely to occur in cement paste cured under ordinary conditions. Gyrolite, or similar phases not described here, could possibly form in autoclaved cement-silica paste products.

The structure of the mineral tobermorite, of approximate composition $C_4S_5H_5$, as worked out by Megaw and Kelsey [62], contains discrete 3-metasilicate chains arranged in a structural unit consisting of two sheets of parallel chains superimposed in such a way that the free OH–OH edges of 7.3-A spacing are pointing outwards and are parallel to the plane of the layer thus formed. Calcium ions are accommodated in internal positions in the planes of the free OH—OH edges of 3.65-A spacing, replacing all the protons. This arrangement corresponds to a C/S ratio of 2/3, or somewhat smaller than the ratio observed in natural tobermorite minerals. The positions of additional Ca and OH ions, and water molecules, were left undetermined, but the authors state that the inclusion of these groups in the calculations is not very likely to destroy the established agreement between observed and calculated X-ray intensities. These groups can well be accommodated in lattice positions between the protruding OH—OH edges, which form a very open layer surface network of approximately hexagonal symmetry.

Another, and completely different structure model for tobermorite has been suggested by Mamedov and Belov [63]. The essential element of this structure is a silica layer formed by polymerization of two sheets of Si_6O_{17} xonotlite chains, each double chain in one sheet sharing tetrahedral corners with two chains in the other sheet. The resulting corrugated silica layer has a unit cell of about 11.3 by 7.2 A, and the composition $Si_{12}O_{31}$. Ten Ca ions per cell are accommodated within and between layers, the C/S ratio thus being 5/6. This structure is believed to expand in a direction perpendicular to the layers in the presence of excess water, by means of a process of diffusion of sheets of water molecules entering interlayer positions.

Even in the case of the fibrous C–S–H compounds C_4S_3H, foshagite, and $C_2SH(B)$, hillebrandite, two different structure models have been proposed. Gard and Taylor [64, 65] postulate a general formula $C_{3+n}S_3H_n$, with n between 0 and 3, for the series wollastonite-foshagite-hillebrandite. The structures of the hydrated compounds are derived from the wollastonite structure by splitting up the layers of single chains into bands and replacing missing valencies by OH ions. Mamedov and Belov [66, 67], on the other hand, are of the opinion that the structures of these compounds can be described in their essential features as association complexes of xonotlite chains and CH columns (foshagite) or CH layers (hillebrandite). However, results obtained recently in an analysis of the foshagite structure, quoted by Taylor (see review paper of this Symposium) are definitely in favor of the structure containing single 3-metasilicate chains, at least in the case of foshagite.

Tobermorite Phases

At the London Symposium, tobermorite was hardly recognized as more than the name of a mineral among many others within the C–S–H system, of rare occurrence in nature and of unknown significance in relation to cement hydration.

It was soon recognized, however, that the naturally occurring mineral was in certain features strikingly similar to the synthetic materials observed in the low-temperature region of the C–S–H system. The existence of a *C*-face-centered, pseudo-unit cell of probably orthorhombis symmetry and of approximate dimensions 5.6 by 3.6 A is the most obvious property common to different tobermorite phases of widely varying C/S ratios. Further, both natural and synthetic tobermorites are composed of layer-lattice structures in which fibrous elements can also be discerned, and the basal spacings of which have been found to vary with the content of water within a certain range of spacings, about 9 to 14 A. Specifically, the value 11.4 A has been used to characterize well-crystallized tobermorite of low C/S ratio. The basal spacings may be constant, or may increase or decrease with the ambient water vapor pressure, depending on the type of tobermorite. The latter properties place the tobermorite phases in a class by themselves among the C–S–H compounds. The similarities to certain types of clay minerals have also been emphasized [68, 69].

Observations on the microstructural properties and particle habits of tobermorite phases have been reported in numerous papers. Owing to large variations in the conditions of formation of the materials studied, such as differences in temperature, composition of raw materials in synthesis mixtures, time of processing, water-to-solid ratio., etc., any attempt to summarize the hitherto observed data in a few simple statements will necessarily leave many observations unexplained.

In general, and especially regarding the colloidal compounds formed at temperatures below about 100 °C, a distinction is made between tobermorite products obtained in two ranges of C/S ratio, viz. the CSH(B) type in the range 0.8 to 1.33 C/S, and the C_2SH_2 type in the range 1.5 to 2.0 C/S [70, 30]. Alternatively, other limits for these C/S ranges have been assumed, e.g., 0.8 to 1.5 and 1.7 to 2.0, respectively [71]. It seems probable that in batches of average C/S ratio about 1.5 both phases are present, or that transitional phases exist. On the whole, the common phase rules of reaction chemistry are hardly applicable to these ill-crystallized and inhomogeneous nonequilibrium solids. The scarcity and diffuse character of XD and ED reflections observed for some CSH(B) and C_2SH_2 phases are indicative of a comparatively low degree of order in the arrangement of parallel-oriented $(SH)_3$ chains and CH complexes, and regions of regularly crystalline lattice formation may extend over only a few unit cells in some directions. Observed variations in particle habits for different C/S ratios may imply that the $(SH)_3$ chains are longer and more isolated from each other in fibrous particles, shorter and more aggregated in coherent sheets in layerlike particles. There is even a remote possibility that the established agreement between the unit-cell dimensions of CSH(B) and well-crystallized tobermorite is fortuitous. An example of two radically different ways of arranging a given number of ionic groups within the same frame is afforded by the structures suggested by Megaw and Kelsey, and by Mamedov and Belov, described in the preceding paragraph.

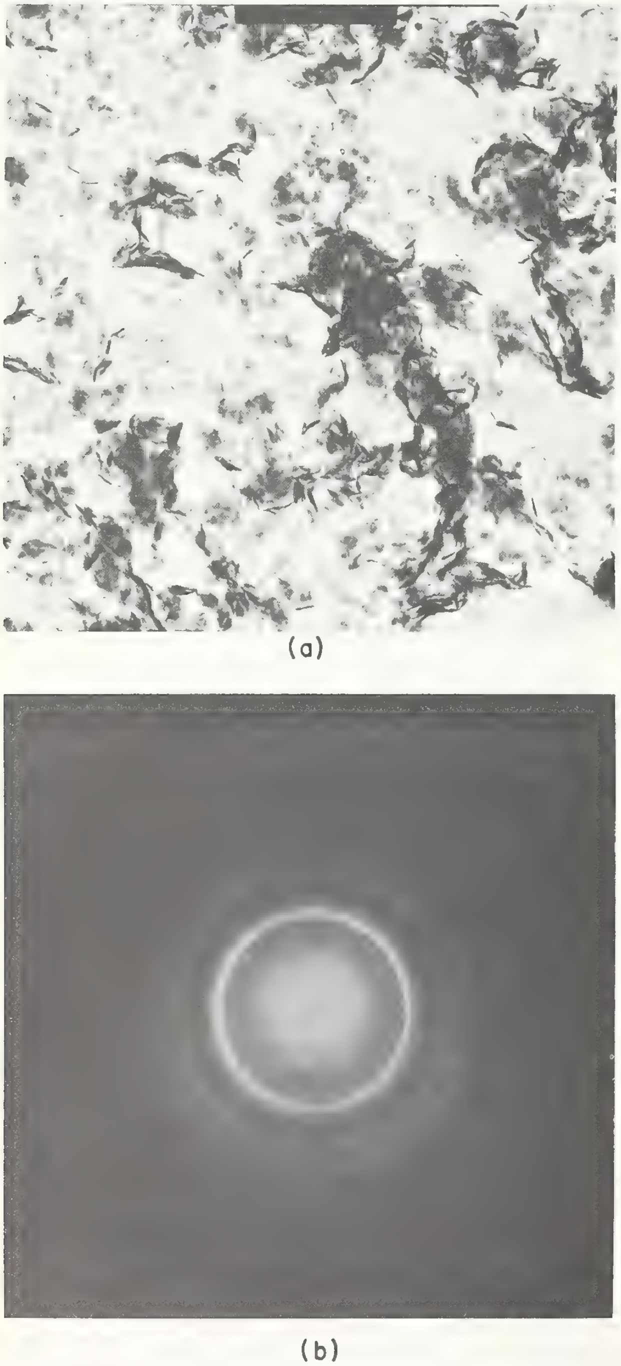


FIGURE 8. *(a) CSH(B) foils and plates, C/S ratio about 1.1, precipitated from a* Ca(OH) *solution containing about 3.8 mM/liter. (b) Electron diffraction pattern of material shown in figure 8a.*

Finally, the high-temperature exothermic peak in DTA diagrams, the variation in temperature and height of which has been used to distinguish in a reproducible way between compounds of different C/S ratios [70], is of dubitable significance when it comes to recognizing these compounds as crystallographically distinct species.

Similar ideas on the CSH(B) and C_2SH_2 structures have been expressed by Taylor [72], and by Assarsson [73] in a discussion on what he calls "phase B", the cryptocrystalline substance formed as a metastable phase prior to the crystallization of distinct compounds in hydrothermal reactions of lime and silica at 120 to 160 °C.

The most commonly observed particle habit of CSH(B), tobermorite, is that of thin sheets or foils, estimated to be only one or two molecular units thick in extreme cases. These particles are also easily deformed, and appear mostly as large conglomerates of crinkly foils. The first EM observation of such crinkly foils was made by Eitel [19] in a product formed in the reaction of a CH solution with an SH hydrosol. Different varieties have later been observed in several EM studies [70, 30, 23, 26, 74, 75]. Gaze and Robertson [76] report the extensive formation of crinkly foils of tobermorite in mixed portland cement-asbestos pastes produced by low-temperature foaming. It seems probable that silica dissolved from the asbestos component and reacting with the lime solution can have contributed to the formation of a product having a C/S ratio in the CSH(B) range. Similar compounds were also observed [77] in lime-quartz paste mixtures of low overall C/S ratios, cured at temperatures of 100 °C and above, but in some products of very low C/S ratio (about 0.4) and cured at 165 °C the paste aggregates consisted of decidedly fibrous or lathlike elements. The crinkly-foil type of CSH(B) appears to be predominant in the pore surfaces of the cement-paste specimens prepared by Bernard [14], using a special technique of preparation. These formations, termed monocalcium silicate hydrate by Bernard, were frequently observed to occur together with acicular particles, and thickened in the course of hydration, forming dense, opaque aggregates.

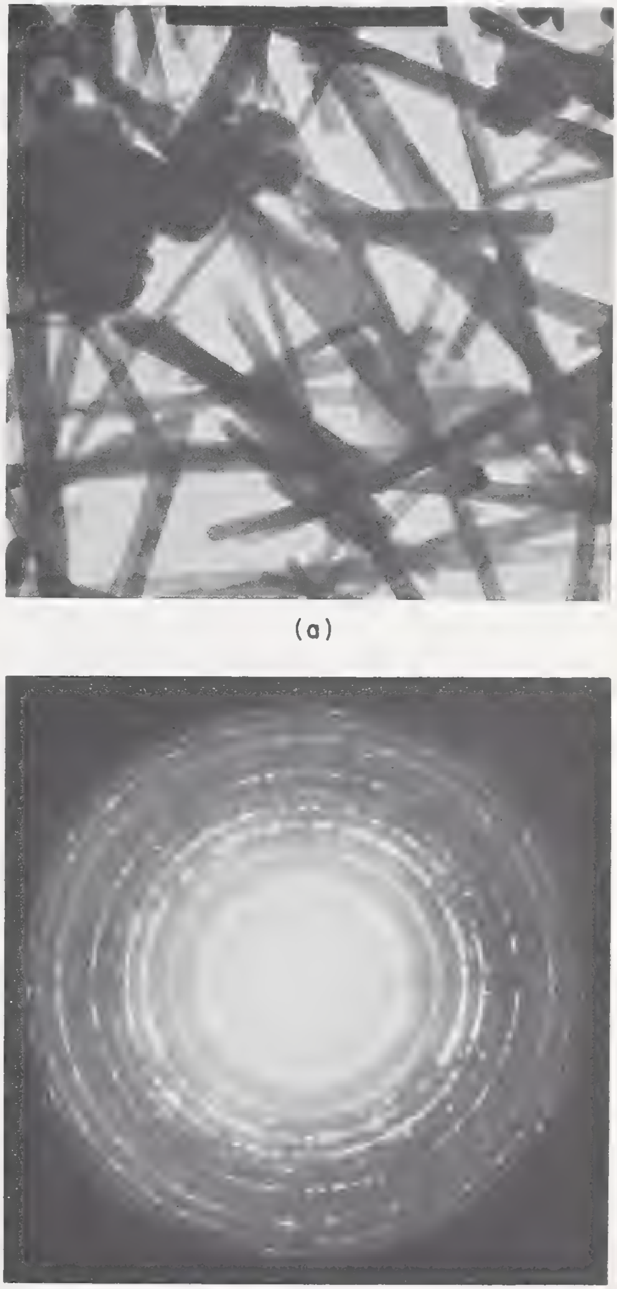
One form of CSH(B) is shown in figure 8 a, b. It consists of small, and comparatively flat, platy particles, together with crinkly foils, and gives a well-developed ED ring pattern of CSH(B)(hk) reflections. The C/S ratio is about 1.1, reached in a CH solution of about 3.8 mM/liter.

The appearance of foils persists almost throughout the whole range of concentration of CH solution phase, except in the immediate vicinity of saturation where a finely fibrous or needlelike growth is promoted [23]. It is questionable if a transformation from CSH(B) to the C_2SH_2 phase can be achieved in temporarily supersaturated solutions. However, Kalousek and Prebus [30] report the formation of a mixture of 1.33 C/S CSH(B) foils and a high-lime solid in the form of coarse, bundled fibers, in a 1.5 C/S batch processed at 60 °C. Fascicular aggregates of fibers, considered to be the characteristic habit of C_2SH_2, have been observed in the products of hydration of C_3S and β-C_2S [78, 23, 71, 79] (cf. also review paper by Brunauer and Greenberg, this Symposium). Similar formations are also common in some varieties of hardened cement pastes, where they can be expected to contribute to the formation of a rigid gel structure (cf. below).

The tobermorite compounds formed at elevated temperatures (approximate range 110 to 170 °C) generally exhibit more characteristic crystalline habits. The low-lime phase, of C/S 0.8 to about 1.2, forms large, flat plates, estimated to be of the order of 10 to 20 unimolecular layers in thickness [80, 81, 82, 70, 77]. A consequence of the more or less regular superposition of layers is that (hkl) reflections and strong basal reflections occur in the XD powder diagrams, which agree well with those obtained from certain natural tobermorites. ED single-crystal diagrams fully confirm the symmetry and dimensions of the postulated unit cell, but are sometimes indicative of polymorphic stacking disorder of the same type as is observed in clay minerals. The transformation from CSH(B) foils, estimated from specific-surface-area measurements and from their transparency to electrons to be only two or three molecular units thick [28, 77], to tobermorite plates is accompanied by a large decrease in specific surface [70].

With increasing C/S ratio the high-temperature tobermorite phases tend to become increasingly fibrous. An electron micrograph from a 1.25 C/S tobermorite prepared at 150 °C shows long, straight rods together with thin plates splitting up into lathlike particles, and the corresponding 1.5 C/S phase consists entirely of long, straight, lathlike or tubular crystals [30]. Ribbonlike crystals of similar appearance are shown by Akaiwa and Sudoh [82], and have also been observed to form slowly during prolonged boiling of afwillite–CH slurry mixtures resulting from ball-milling of C_3S in water [28, 26] (fig. 9 a,b). ED single-crystal diagrams indicate the existence of a simple (not face-centered) base unit cell of dimensions 5.2 to 5.4 by 3.6 A, although reflections with h+k odd are generally weaker. A possible way of interpreting these data in terms of structure would be to suggest the presence of a layer lattice element of the unsymmetric SH—CH type, instead of SH—C—SH, as in the tobermorite structure model proposed by Megaw and Kelsey. Of special interest is the decrease in unit distance across the chains, which leads to a displacement of, e.g., the strong hk=11 reflection from about 3.07 A, normally observed in tobermorites, to about 2.96 A. The formation of mixed-layer compounds may account for the general blurring of the strong ED reflections in the 2.8– to 3.1–A range, observed in different constituents of hardened cement pastes, as is further exemplified in later sections of this review.

Of considerable interest in this connection is the study made by Kalousek [83] of tobermorite prepared with varying amounts of alumina present in the reaction mixture. He found that it was possible to replace a limited amount of Si ions by Al ions in tetrahedral positions, 4 to 5 percent A per $C_{4-5}S_5H_5$ tobermorite. Increasing the amount of alumina in the mixture above about 5 percent



(a)

(b)

FIGURE 9. *(a) High-temperature tobermorite phase formed by boiling of an afwillite*-Ca(OH) *slurry prepared by ball-milling* C_3S *in water. (b) Electron diffraction pattern of material shown in figure 9a.*

resulted in the formation of increasing amounts of the hydrogarnet compound C_3ASH_4 (or possibly $C_3AS_2H_2$) as a second phase. The crystals of the Al-substituted phase showed a marked decrease in size but were still of a platy habit, and the XD powder patterns exhibited slight changes from those of tobermorite without substitutions. If observations of a corresponding limit of substitution of Al ions could be made also in the case of the low-temperature compounds, CSH(B) and C_2SH_2, a method would be afforded of testing the postulate of relative independency of reaction with water of the C–S and C–A–F clinker constituents. This postulate, once advanced by the cement chemists as a kind of working hypothesis for lack of evidence to the contrary, seems to have acquired a degree of general validity which may not be altogether justified.

Some considerations and evidence on the probable incorporation of silica groups in the hydration products of the C–A–F and C–$\bar{S}$ constitutents of cement were presented in the previous section. Concerning the question of alumina in the C–S–H gel phases, it can be shown by a simple calculation that in a cement containing alite of a composition approximating the well-known Jeffery formula, $C_{54}S_{16}AM$, the alumina held by the alite itself would correspond almost exactly to a 5 percent substitution limit in the tobermorite phase formed from this alite, thus no alumina would be exchanged with the other clinker constituents. On the other hand, some alumina in solution may enter into the C–S–H gel phase formed from belite, which is assumed to contain no alumina initially. In view of the low rate of hydration of β-C_2S, it would seem that only a very small amount of alumina is involved in this process, at least in the early stages of setting and hardening. It is conceivable, however, that the presence of aluminate ions in the liquid phase may accelerate the hydration of belite considerably.

Structure Elements in Colloidal Tobermorite Phases

It is a matter of some interest to speculate on the possible relationships between the CSH(B) and C_2SH_2 structures and the structure models proposed for tobermorite, as described earlier. As has been shown, sheetlike habits predominate in CSH(B) particles, in spite of the probable existence of one-dimensionally coherent lattice elements in them. It would appear, therefore, that the Mamedov-Belov structure model, containing polymerized silica layers, is the most likely alternative. However, this structure has a comparatively rigid, self-contained character, and it seems difficult to imagine an incorporation of extra lime to take place without increasing the unit layer distance to impossible values. This lattice may well apply to certain types of well-crystallized tobermorite, but silica layers of a correspondingly high degree of complexity and polymerization are unlikely to be present in the ill-formed structures of CSH(B) and C_2SH_2. The Megaw-Kelsey structure model is, on the whole, more flexible, and can be modified theoretically in various ways in order to fit observed data without violating the principles of arrangement of structural elements inherent in this model. One such hypothetical modification, the unsymmetric SH—CH layer, has already been described. This layer has a C/S ratio of 4/3. It is perhaps fortuitous that Kalousek and Prebus set a limit in the range of existence of CSH(B) at 1.33 C/S, or that Pressler, Brunauer, and Kantro [84], in extracting lime from a mixture of lime and 1.5 C/S tobermoritic material obtained in a hydrated C_3S paste, found an abrupt break in the rate-of-extraction vs. time curve, occurring at 1.34 C/S in the tobermorite phase. Certain observations of basal spacings decreasing with C/S ratios increasing in the 1.0 to 1.5 range [23] are, however, more easily explained by a mechanism of structural change involving the removal of SH elements from the layers, rather than by an addition of CH elements to a layer core of constant composition. The accommodation of additional C—H complexes in the two structural "holes" (per 11.2 by 7.2 A unit cell) between the ridges of the silica sheet would bring the C/S ratio up to the maximum value of 2.0, assumed for C_2SH_2.

The electron-optical evidence presented in a recent paper by Gard, Howison, and Taylor [85] fully confirms the description given above of the various morphologic habits and other properties of the synthetic tobermorite phases, and in addition furnishes data on the modes of transition between different particle habits and on transformations to dehydrated C–S compounds on heating. Two observations seem to be of special interest. One of these is the suggestion of the existence in C_2SH_2 of unsymmetrical SH—CH layers coupled together by C—H layers, in analogy to halloysite among the clay minerals and agreeing with the considerations put forth in this review. The other observation is that of the common occurrence in well-crystallized tobermorite plates of aggregates stacked with the *b* axes of separate layers rotated through approximately hexagonal angles. According to the authors, this suggests that the surfaces of tobermorite crystal elements consist of CH layers rather than SH chains. However, it seems that also the open, nearly hexagonal structure of the layer of SH chains of the Megaw-Kelsey lattice model would equally well permit a fit between adjacent units with mutually rotated directions of chains. However this may be, it can be assumed that such modes of rotational superpositions would occur frequently for subcrystalline tobermorite unit layers crystallizing in the very narrow gel spaces of a cement paste. An aggregation of the type suggested is likely to cause restrictions in particle size and to favor the development of small particles tending to assume the habit of flakes rather than fibers. Further, it would be almost impossible to detect any crystalline properties in such formations by means of diffraction methods. We have here a possible explanation of the fact, exemplified in later sections of this review, that in some cement pastes of normal data the expected formation of fibrous structures of C_2SH_2 tobermorite largely fails to occur.

It must be emphasized that the ideas put forth in the last paragraph are of a highly speculative nature, representing only one of a few alternative ways of reviewing the object matter. Buckle and Taylor [29] regard the problem of structure formation in ill-crystallized tobermorite from a somewhat different angle. They assume a structure composed of a mosaic of crystal elements of extremely small size, with a short-range undulation of structure type between pure CH and pure tobermorite. It seems that this is merely an alternative way of describing the molecular texture of an ill-crystallized composite gel material, not a fundamentally different conception of the structure.

Another theory of the relationship between structure and C/S ratio of tobermorite gel phases is advanced by Taylor and Howison [68], supported and further developed by Brunauer and Greenberg (this Symposium). According to this theory, the degree of polymerization of the metasilicate chains decreases with increasing C/S ratio. It is assumed that, at certain intervals of the chain, the ionic bond connection is interrupted, due to the absence of $Si(OH)_2$ groups described earlier in this paper as protruding OH—OH edges of the Megaw-Kelsey model structure for tobermorite. Instead of a missing $Si(OH)_2$ group, one Ca ion and possibly one water molecule are assumed to enter nearby sites in the lattice. Complete replacement would correspond to a C/S ratio of 1.75.

This theory, if developed in further detail, seems to afford interesting possibilities for a revision of current ideas on the C–S–H gel structure, as reviewed earlier in this paragraph. However, conclusive evidence is still largely missing, and it is obvious that further experimental work, with the purpose of obtaining a confirmation of structural theories or a better resolution of the tobermorite gel structure, will meet with great difficulties. Because of the apparent importance of some form of the tobermorite phases for the formation of an integrated gel structure in hardening cement paste, it seems urgent to make some attempts at forming a conception of the various arrangements of ionic groups in the structures of these compounds, specifically the crystal patterns in the outer surfaces.

Afwillite

Although afwillite is not very likely to develop hydraulic properties, owing to the essentially noncolloidal character of its crystals, it has nevertheless been mentioned in the literature as a possible constituent of cement hydration products.

Judging from evidence obtained in microscope studies, Nacken [86] suggested that in the successively proceeding hydrolysis of C_3S crystals, first $C_2SH(B)$, hillebrandite, then $C_3S_2H_3$, afwillite, and possibly CSH_2, plombierite, are formed as surface layers on the anhydride crystals. Other observations, made in EM studies by Zhuravlev (unidentified reference given by Schwiete and Müller-Hesse [31]), indicated the formation of needlelike crystals, probably of afwillite, in the early stages of hydration of calcium silicates. However, too much importance should probably not be attached to these observations which are difficult to reconcile with later findings.

In reports by Swerdlow, McMurdie, and Heckman [87, 88], dealing in particular with products obtained by ball-milling of C_3S slurries, the suggestion is made that afwillite could be a hydraulically active constituent of hardening portland cement pastes, probably constituting, together with crystalline CH, the product of ultimate equilibrium in fully hydrated C_3S paste. The active ingredients of the observed gel structures were considered to be extremely small, discrete gel globules conglomerated in spherical clusters, and a theory was advanced explaining tentatively the mechanism of hydraulic hardening as being a process of coalescence and intergrowth of the spherical clusters. The XD patterns given by extracted fractions of the small, discrete particles agree with that of afwillite, whereas the ED patterns from the surfaces of the large agglomerates are said to resemble the diffraction patterns given by tobermorite and possibly hillebrandite.[2]

In order to verify these observations, which lead to a conception of structure formation in cement paste differing considerably from those of other commentators [8], the present author examined the hydration products in C_3S slurries, ball-mill-hydrated in a similar way but omitting the subsequent dispersion by ultrasonic treatment [26].

The fully hydrated product was composed of about equal amounts of CH crystal plates, sometimes aggregated in large, flaky structures, and aggregates of rather large and thick afwillite crystals, of the appearance of rhombic slabs with somewhat rounded corners (fig. 10). Owing to the intimate mixture of CH and afwillite, the ED diagrams consist of mainly CH spot-ring reflections, whereas the afwillite crystals are generally too thick and well-crystallized to give ED effects. However, in many diagrams diffraction spots not belonging to the CH pattern are observed, especially at about 6.48, 5.04, 4.12, 3.20, 2.82, and 2.14 A, coinciding approximately with some strong, or medium strong, reflections of afwillite. A few other strong XD reflections

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[2] In the opinion of the present author, the distribution of intensities and the relative spacings of the ED patterns shown are in good agreement with those of ED patterns of C, calcium oxide. For lack of numerical data, no absolute comparison can be made. However, it can be pointed out here that C patterns frequently appear, even at low levels of electron irradiation intensity, in EM studies of freshly precipitated hydration products which have not yet had time to stabilize.

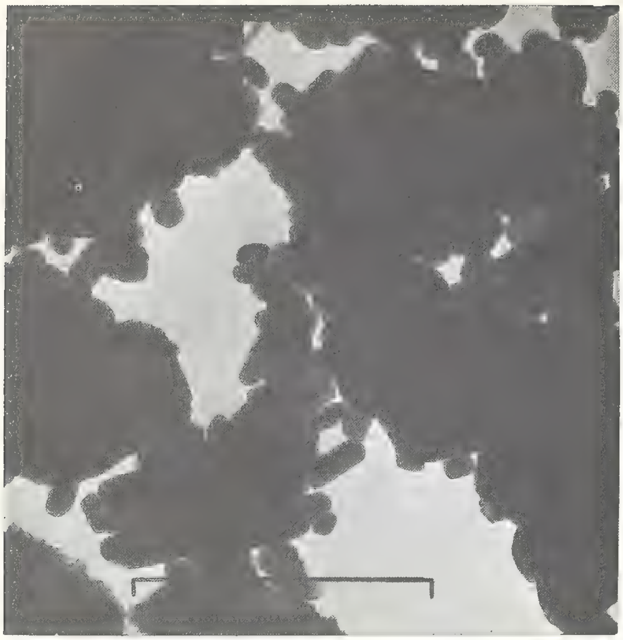


FIGURE 10. *Calcium hydroxide plates and aggregates of afwillite crystals formed by ball-milling* C_3S *slurry without subsequent ultrasonic dispersion.*

of afwillite are not observed in ED patterns, but it should be pointed out that one can never expect a complete agreement in weak spot patterns of this erratic character. The XD diagram contains the spectra of both CH and afwillite.

These results indicate that the nature of the crystallization processes taking place in the course of hydration of cement can be changed radically by applying a procedure of mixing involving prolonged and intensive mechanical treatment. Since both C_3S and afwillite contain isolated SiO_4 tetrahedra in their lattices, it seems natural to explain the effect of ball-milling by assuming that it prevents the SiO_4 groups from polymerizing into chains, or breaks up any chain structures incidentally formed. It can be noted that β-C_2S slurries, similarly treated, yield tobermorite materials in the hydration products [28]. This result indicates that the presence of a sufficiently large excess of Ca ions in the mixture is also required, in order to keep silica groups from combining.

It can be further supposed that the application of high-power ultrasonoration may lead to complete peptization and destruction of crystalline structures, as is indicated by the observations just described.

Xonotlite, Hillebrandite, and Tricalcium Silicate Hydrate

The morphologic habit of xonotlite, of composition CSH_n, with n variably reported to be 1/3, 1/5, or 1/6, has been observed by Kalousek [80] and by Akaiwa and Sudoh [82]. This mineral consists of long, slender, fibrous or lathlike crystals.

Similar habits are exhibited by $C_2SH(B)$, synthetic hillebrandite, which also forms aggregates of broom-shaped or fascicular character, resembling C_2SH_2 [82]. An electron micrograph of the natural mineral shows aggregates of particles of fusiform shape, giving ED spot patterns indicative of three-dimensional crystallization [23].

Tricalcium silicate hydrate, $C_3SH_{1.5}$, is of considerable interest because of its occurrence in C_3S pastes cured at different temperatures after long periods of curing even at temperatures as low as 50 °C, as observed by Buckle and Taylor [29]. These authors state that "although persistent, $C_3SH_{1.5}$ is probably not a thermodynamically stable product below at least 170 °C. The restrictions on atomic transport and rearrangement in pastes cured at these relatively low temperatures possibly favour formation of compounds with the same Ca/Si ratio as the starting material. After the $Ca(OH)_2$ has had time to segregate into relatively large crystals, tricalcium silicate hydrate does not form below about 200 °C".

No sign of the presence of $C_3SH_{1.5}$ could be detected in electron micrographs of C_3S pastes cured for long periods at room temperature. Crystals of $C_3SH_{1.5}$ produced at high temperatures showed characteristic habits of long needles or rods, often with foil-like or tubular extensions at the ends [53]. Single-crystal ED patterns can be indexed on the basis of a unit cell of hexagonal symmetry, with the *c* axis of length about 7.5 A (i.e., slightly larger than the unit distance in the 3-metasilicate chain) parallel to the fiber axis. It remains to find a lattice structure compatible with this rather peculiar relationship between morphologic properties and crystal symmetry.

C_3S and β-C_2S Suspensions and Pastes

General Considerations on Hydration Reactions

The extensive literature on the reaction chemistry of the hydration of C_3S and β-C_2S, the two main ingredients in portland cement, will not be reviewed here. It may suffice to state that these compounds give mainly the same hydration products at temperatures up to at least 100 °C, viz., colloidal or microcystalline tobermorite phases, C_3S producing one extra mole of CH per formula at complete hydration [28]. It is observed that C_3S hydrates much more rapidly than β-C_2S. In matters pertaining to the development of microstructures in the hydrated phase, the ideas put forth by van Bemst [71, 89] can serve as a basis for further discussion.

In general agreement with the theories on cement hydration once developed in the classical works of Le Chatelier, van Bemst observes that the silicate constituents are dissolved superficially, and that CSH (B) is precipitated in the outer solution phase thus formed. This reaction is rapid at first but slows down considerably as the effective Ca ion concentration increases. At a certain concentration of Ca ions in solution, assumed by van Bemst to be normal saturation point (about 20 mM C per liter), but probably in reality far exceeding this value, conditions are favorable for the formation of C_2SH_2. This phase forms directly on the surfaces of residual anhydride cyrstals. The precipitation of the C_2SH_2 phase proceeds at a comparatively high rate, and the decomposition of the anhydride compounds is again accelerated.

A consequence hereof, according to van Bemst, is that paste hydration of the silicates proceeds more rapidly than hydration at higher water-to-solid ratios. In the case of paste and slurry hydration of β-C_2S at 100 °C, a similar observation is made by Funk [79], who noticed that complete hydration of β-C_2S at $w/c = 0.5$ could be reached in about 10 days, whereas at $w/c = 3$ the product was only about 50 percent hydrated after the same time. In addition, further reaction seemed to proceed at an exceedingly slow rate.

A possible explanation of these phenomena would be that the CSH (B) foils, if formed in larger amounts with excess water, adhere to the anhydride silicate surfaces, covering them with a more or less impermeable coating. On the other hand, the fibrous particles of C_2SH_2 type, if once formed, radiate outwards from the surfaces, furnishing paths of easy diffusion of the ionic groups participating in the process of hydration and hydrolysis.

It should be noted, however, that other investigators have arrived at quite different results, indicating that in general the rate (or degree) of hydration tends to increase with increasing w/c ratio. The relative amount of water in a mix is only one among several factors that determine the rate of reaction at various stages of the process of hydration, as is elucidated in further detail by Brunauer and Greenberg (this Symposium).

Observations made by the present author on hydration products formed in C_3S suspensions in water and in lime solutions are mainly in agreement with the conceptions of structure development now described. The solid phase produced by long-time shaking of C_3S-water mixtures of such proportions that a C/S ratio of about 1.7 was reached in a nearly saturated solution (small but undetermined amounts of solid CH modifications were present) consisted of large flocs of foil-like material of a rather open texture, giving ED ring patterns indicating ill-crystallized CSH(B) (3.0- and 1.8-A reflections).

Corresponding hydration products of C_3S suspended in a saturated CH solution were still largely foil-like, but with some foils rolled up to form long and rather thick fibers. This product gave an ED pattern consisting of only one diffuse ring at about 2.8 to 3.1 A. Another phase, observed to be present in small quantity, appeared as fusiform particles consisting of bundles of parallel fibers. The ED patterns were those of calcite, and these particles are therefore pseudomorphs caused by carbonation of the original structure.

Finally, with C_3S suspended in a highly supersaturated CH solution (about 31 mM C per liter), large flocs showing at the edges a feltlike texture of finely fibrous particles were predominant, but considerable quantities of the fusiform particles were also observed. Also present, of course, were large amounts of CH precipitates, of the $\overline{C}$-contaminated type.

The introduction of certain types of surface-active agents in solution can change the rate of hydration and modify the hydration products. This has been shown by Adamovich [24], reporting data from EM studies of C_3S and β-C_2S hydration in suspensions, with or without admixture of small amounts of lignosulfonate (sulfite liquor). He states that the hydration process is considerably accelerated in the presence of the surface-active agent, which also acts as an inhibitor of hydrolysis, especially of C_3S. The hydration products are characterized as fascicular fiber aggregates with splintered ends, strongly resembling C_2SH_2 tobermorite particles.

C_3S Pastes

The products of hydration in C_3S pastes cured for long periods up to more than 5 yr at room temperature, were examined in the electron microscope by Buckle and Taylor [29]. All pastes showed the same structure, that of irregular masses possibly composed of small plates. These aggregates gave no ED pattern, but occasional larger crystalline fragments were identified by means of their ED patterns as CH crystals. The irregular masses are almost certainly very ill-crystallized tobermoritic material. The structure of this material is tentatively described as intermediate between those of CH and tobermorite, with metasilicate anions partially and disorderly replacing OH ions in the CH structure.

No electron-optical data are given by Buckle and Taylor on the C_3S pastes cured for prolonged periods at higher temperatures, but their optical and X-ray evidence seems to indicate that the phase composition, and most probably also the morphologic character, is changing rapidly with increasing temperatures of curing. Some support for this statement is given by observations of structure formations in a C_3S-water suspension boiled for a few minutes [26]. This treatment resulted in the appearance of a mixture of hydrated solid phases of particle habits quite different from those observed under similar conditions at room temperature.

Data on phase compositions of the hydration products of C_3S and β-C_2S hydrated under different moisture and temperature conditions and with various additions of asbestos and quartz, have recently been reported by Berkovich, Kheiker,

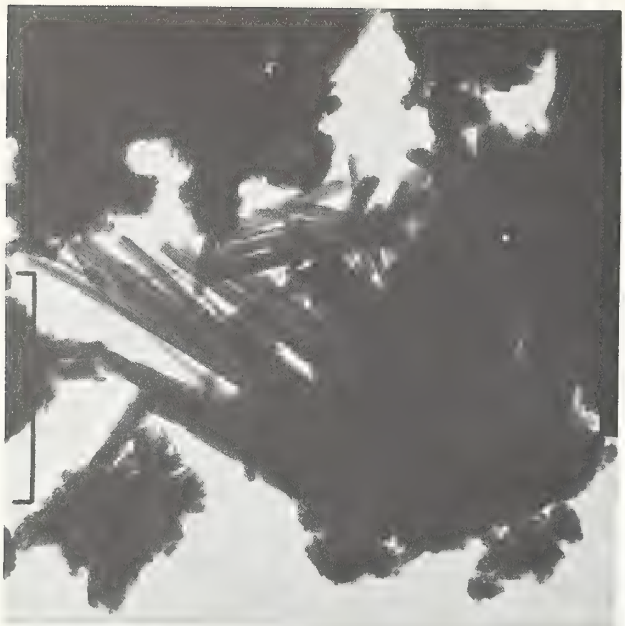


FIGURE 11. *Fibrous tobermorite formed in a fully hardened paste of* C_3S.

Water-to-solids ratio=0.7; age=7 months.

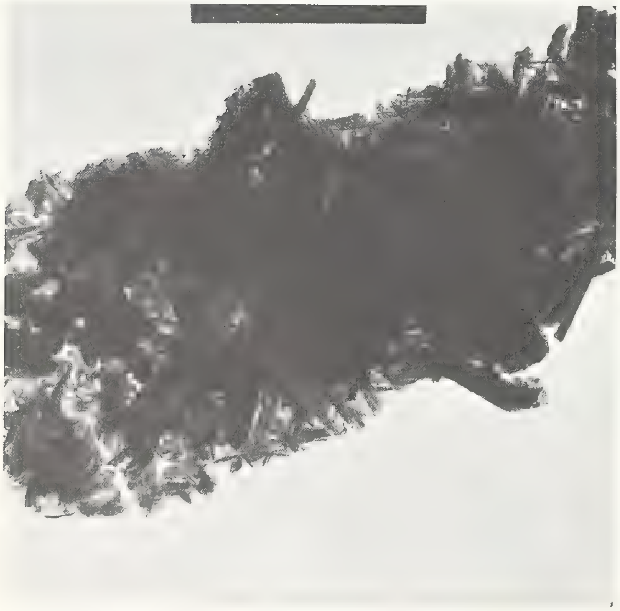


FIGURE 12. *Skeletal framework of elongated particles remaining after brief shaking of dried and powdered fully hydrated* C_3S *paste with water.*

Gracheva, and Kupreeva [90]. With special reference to low-temperature hydrates, it is stated that fibrous C_2SH_2 and CSH(B) can be identified in materials cured at 20 and 60 °C. The mixtures autoclaved at higher temperatures show complex compositions. It can be specially noted that the appearance of $C_2SH(A)$ seems to correspond to a lowering of the mechanical strength of mixed C_3S-asbestos pastes, but the decrease in strength is ascribed to corrosion of the asbestos particles. On the other hand, the formation of CSH(B) in mixed C_3S-quartz powder pastes is connected with an increase in strength.

Some fully hydrated C_3S paste materials (water-to-solid ratio 0.7, age 17 months) produced in the stoichiometric studies made by Brunauer, Kantro, and Copeland [28] were examined by the author [26, 32, 33]. A large part of the material consisted of irregularly shaped agglomerates of small and thin particles, similar to those described by Buckle and Taylor, and showing in ED diagrams at most a very diffuse ring at about 2.8 to 3.1 A. However, a second phase was also observed in about equal amounts. It consisted of long and rather thick needles or rods, obviously composed of bundles of fibers or tubularly rolled sheets, often radiating from a common center (fig. 11). The ED patterns from such aggregates contained a diffuse ring at about 2.9 to 3.0 A, and a mostly weak but sharp reflection at 1.80 to 1.82 A, characterizing these products as fibrous tobermorite. A third phase, that of large and fairly thin plates of CH crystals, easily recognizable by means of their characteristic ED spot patterns, was also found in appreciable amounts.

If the dried and powdered C_3S paste was shaken with water for a very short time prior to the preparation of EM samples, some amount of the irregular masses seemed to dissolve or become rinsed away, revealing in many aggregates a skeletal framework of elongated particles (fig. 12). This observation seems to indicate that the amorphous-looking masses may be aggregated in and around the meshes of a rigid structure which holds them together.

Microstructural elements very similar to those now reported have been observed by Kurczyk [91] in C_3S pastes, hydrated one month at 30 °C. Apart from larger unhydrated particles, the material seems to consist of about equal amounts of finely textured irregular masses, of rather long branched needles, and of thin plates, presumably CH crystals. An addition of small amounts of gypsum to the paste mixture is said to influence the development of hydrated structures in an unfavorable way, but the character of the changes taking place is not clear.

β-C_2S Pastes

The products of paste hydration, at 50 and 100 °C and a water-to-solid ratio of 0.5, of β-C_2S containing additions of small amounts of various stabilizers (to prevent conversion to γ-C_2S), were studied by Funk [79]. These pastes consisted almost entirely of fibrous C_2SH_2-type tobermorite, with minor amounts of CH crystals. The materials prepared at 50 °C were composed of dense aggregates of thin fibers, whereas at 100 °C longer and thicker needles or rods were observed. The C/S ratios in the solid phases varied from 1.7 to nearly 2.0, the materials produced at 100 °C being higher in lime. When β-C_2S was hydrated in water vapor at 100 °C it gave a product composed of loosely aggregated bundles of fine needles. It was observed that the mechanical strength of such products was very low, whereas paste-hydrated β-C_2S materials were quite hard. From this fact Funk concludes that the presence of a solution phase during hydration is essential for the formation of a hardening, integrated structure.

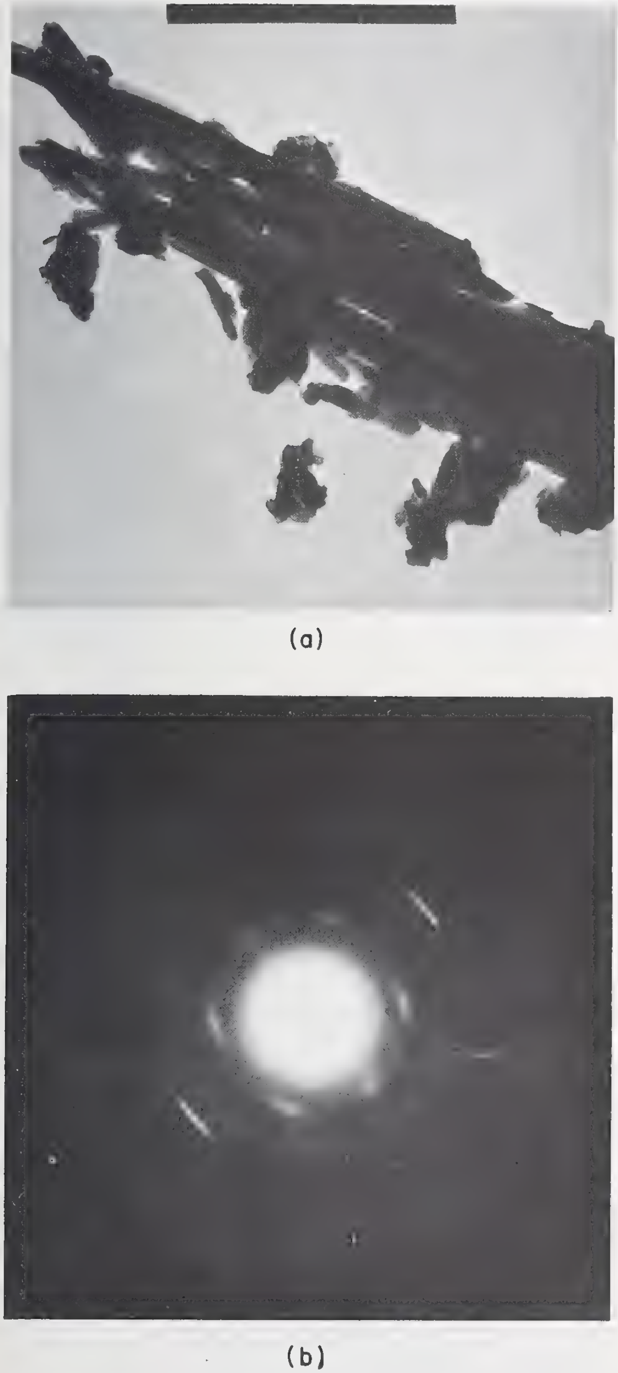


FIGURE 13. *(a) Coarsely fibrous particles from hydrated β-C S paste. (b) Electron diffraction pattern of fibers shown in figure 13a.*

Water-to-solids ratio=0.7. Seventy percent hydrated at 17 months.

The present author examined dried and ground material from β-C_2S paste (water-to-solid ratio 0.7) hydrated at room temperature for 17 months, after which period it was found to be nearly 70 percent hydrated [28]. The microstructures of this material resembled those observed in correspondingly hydrated C_3S pastes described in the preceding section, with irregular aggregates of small, distorted plates as the predominating phase. However, the coarsely fibrous or tubular particles also occurred in appreciable quantities. A bundle of such fibers is shown in figure 13 a, b, together with some irregularly shaped material. The ED fiber pattern consists of six diffuse, hexagonally arranged spot reflections at about 2.95 A, and a sharp streak at 1.83 A (corresponding to $b=7.32$ A along the fiber axis). Occasional large, thin plates of CH crystals were also observed, indicating that some hydrolysis of β-C_2S had taken place.

Considerations on Differences in Structure Development and Hardening Processes

The evidence available on low-temperature paste-hydrated C_3S and β-C_2S seems to show that the phase composition and particle habits are essentially the same in both materials, with the exception that the amount of crystalline CH is considerably larger in C_3S pastes. It is well known that C_3S pastes harden and develop a high mechanical strength much more rapidly than do β-C_2S pastes. It seems natural to assume that the rapid development of a crystallized CH phase at early ages in C_3S pastes is the main factor responsible for this discrepancy in the rate of hardening. This opinion is held by Ershov [92], who concludes that CH participates in the hardening process, and, in particular, that "the basic factor controlling early strength of portland cements should be viewed as the quantitative content of $Ca(OH)_2$ in the products of hydration", whereas "the basic factor controlling strength gain at later periods of hydration is the delayed hydration of C_2S and the continuous process of densification of gel structure"

These views cannot be directly substantiated by the EM data. On the contrary, the crystal plates of CH seem to be easily broken away from the rest of the gel structure, and practically always appear as detached particles with clean surfaces, with no signs of adsorption or bonding of gel material, or of formation of continuous structures by an intergrowth of partially overlapping plates, as is probably the case in hardening lime mortars.

The alternative explanation of the difference in the rates of hardening, that of the generally higher reactivity of C_3S in contact with water, leading to a more rapid development of colloidal C–S–H phases, is of course of a very vague nature. The relative rates of development of the amorphous and the coarsely-fibrous phases during the early stages of paste hardening must first be studied, before any opinion can be formed on the true nature of early hardening and subsequent strength gain in calcium silicate pastes.

Gel Phases in Portland Cement Pastes

Introductory Remarks

Hitherto published EM data on the microstructure of cement paste materials [14, 15, 30, 32, 33, 34, 88] have established in broad outline the character of various constituents of the hardened cement gel, and there seems to be reason to hope for major contributions to the systematic solution of important problems relating to this subject to be forthcoming in the near future. For the present review, the author finds it convenient to use mainly his own observations on various paste materials which, however, have not been prepared in a systematic way, but rather selected from available samples of pastes of different description [26].

Observations on Pastes Hardened at Normal Temperatures

Since about 70 to 80 percent of portland cement of normal composition consists of a mixture of alite and belite, the impure clinker modifications of C_3S and β-C_2S, it can be expected that the predominant phases in hardened portland cement pastes would be very similar to the gel phases observed in the pure silicate pastes. This is found to be the case. It can be stated that by far the largest part of the cement pastes examined consists of exceedingly ill-formed, colloidal products, in which it is sometimes difficult to discern any definite morphology. The remainder of the pastes consist of relatively large-sized plates of CH and C–A–H (possibly C_4 (A, F, $\bar{S}$)·aq.) crystals, the properties of which have already been described, and which are always present in some quantity, mostly small.

The lightly ground paste materials are mostly found to be composed of rounded, irregular aggregates of diameters generally ranging between 0.5 and 2 μ. It is supposed that these aggregates correspond to the initial cement particles, and that grinding or milling operations have the chief effect of splitting the material along zones of contact between hydrated particles.

As in pure C_3S and β-C_2S pastes, the particulate structure in the interior of the aggregates is a mixture of fibrous or acicular elements and elements of the shape of small and thin, rounded flakes, of the order of up to a few hundred A in diameter. The latter phase is predominant, and the fibrous phase has in general a finer and more distorted texture than in pure silicate pastes.

The ED diagrams from representative aggregates are extremely weak and diffuse, mostly showing only a broadened reflection at about 2.7 to 3.1 A. Whenever the fibrous phase is present in noticeable amounts, a weak but sharp fiber reflection at 1.81 to 1.82 A can also be detected. These diffraction effects are, exactly as in XD patterns, the only reflections recorded, except spot reflections from CH and C–A–H plates, in case such particles occur in the image field.

Figure 14 shows a representative aggregate in a Type I (ASTM) cement paste (specific surface 1,800 cm^2/g in cement, w/c 0.55, 5 months old). Figure 15 is taken from a similar paste (w/c 0.65, 5½ yr old). Fibrous or bundled structures are visible in both pastes, but the more amorphous masses predominate. In figure 16, from the same paste as figure 15, heavy bundles of long fibers are seen together with finely textured material. Such formations are, however, not very common. In rare cases, similar particles have given ED patterns consisting of six hexagonally arranged, diffuse 3.0-A spots plus a fiber reflection streak at 1.81 A, similar to the pattern in figure 13b.

Pastes made up with other types of cement were in general found to be very similar to the Type-I cement pastes. Figure 17 represents gel-structure elements from a Type-IV (low-heat) cement, higher in β-C_2S and lower in C_3S and C_3A (2300 cm^2/g, w/c 0.6, 7½ yr old). Figure 18 shows a type of aggregate consisting of very fine (less than

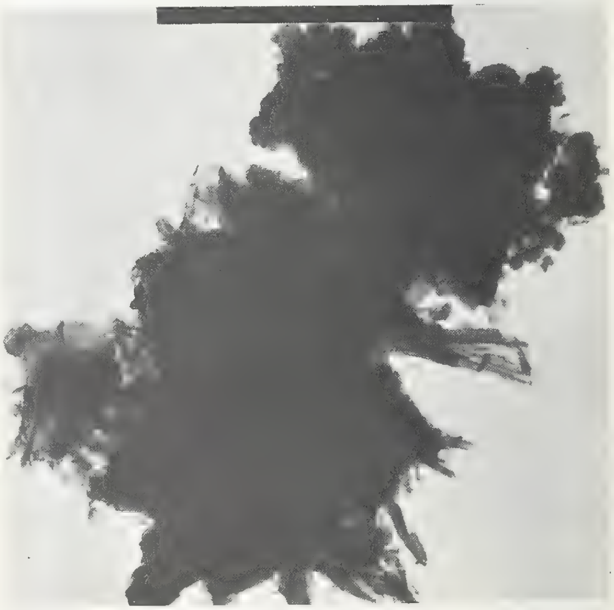


FIGURE 14. *Representative aggregate from lightly ground hydrated Type I cement paste.*

w/c=0.55; age=5 months.

100-A wide) fibers appearing as a common constituent, together with flaky aggregates, in a paste of Type III (rapid-hardening) cement, high in C_3S and ground slightly finer than normal (2,500 cm^2/g, w/c 0.6, 7½ yr old). The ED patterns are indistinct, in spite of the fibrous appearance.

An effect of higher degree of fineness of grinding is exemplified in figure 19, originating from a paste prepared from the 8000-cm^2/g fraction of an ordinary Type I cement (w/c 0.7, 2½ yr old). The increase in porosity and the exceedingly small size of particle elements of the gel aggregates in this paste are characteristic features. The tendency to formation of fibrous habits is small. The large and thin plates also visible in this micrograph are crystals of the C–A–H hexagonal-plate phase.

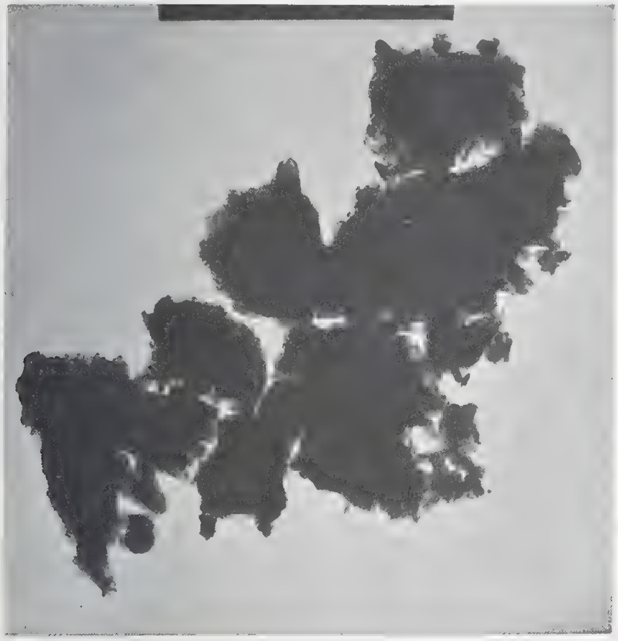


FIGURE 15. *Representative aggregates from lightly ground hydrated Type I cement paste.*

w/c=0.65; age=5½ yr.

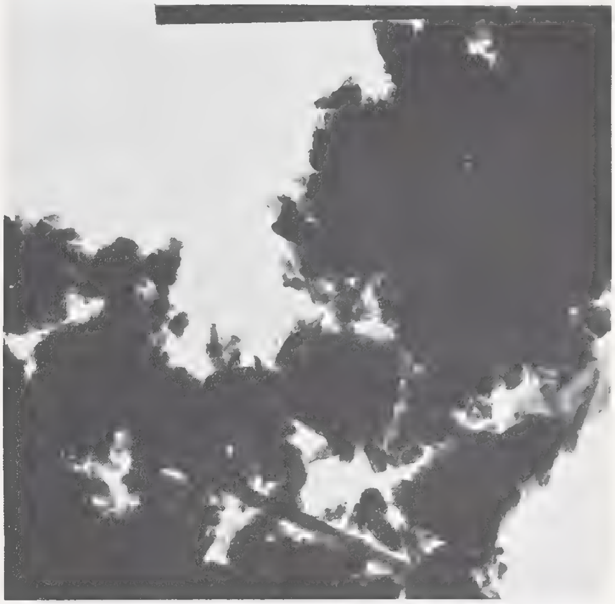


FIGURE 17. *Gel-structure elements from Type IV cement paste.*

w/c=0.6; age=7½ yr.

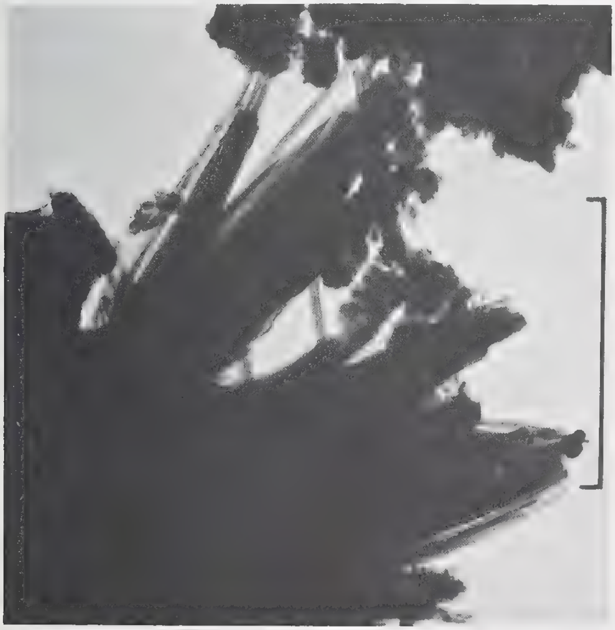


FIGURE 16. *Relatively rare fibers from lightly ground hydrated Type I cement paste.*

w/c=0.55; age=5 months.

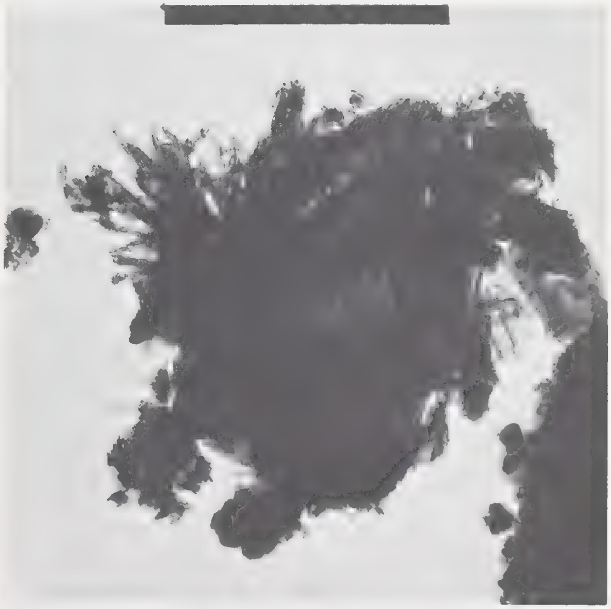


FIGURE 18. *Representative gel aggregate from Type III cement paste.*

w/c=0.6; age=7½ yr.

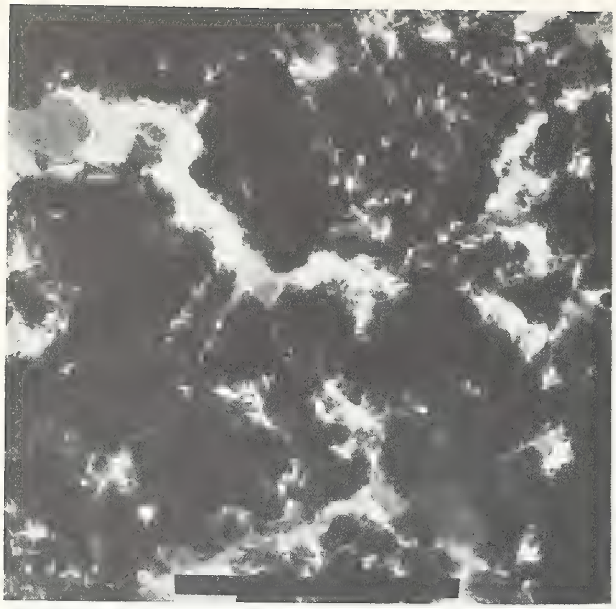


FIGURE 19. *Representative gel aggregates from a paste prepared from the 8,000-cm²/g fraction of Type I cement.*

w/c=0.7; age=2½ yr.

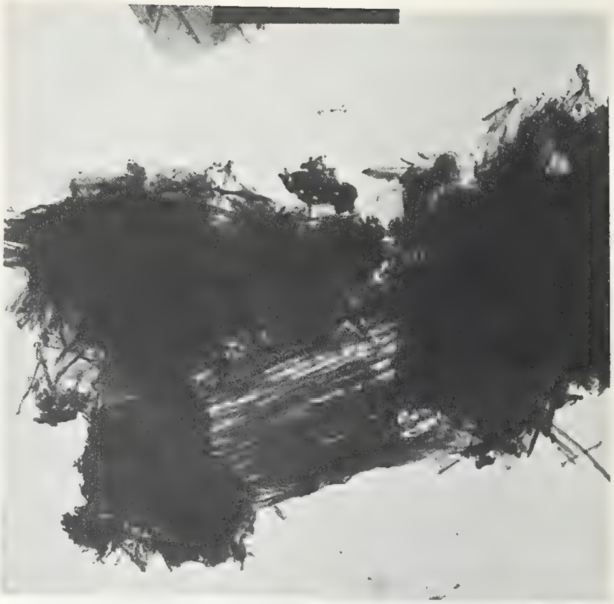


FIGURE 20. *Representative fiber bundles from a paste prepared from the 8,000-cm²/g fraction of a Type I cement.*

w/c=1.5; age=3 yr.

The same high-surface-area cement was used in preparing paste samples with the exceedingly high w/c ratio of 1.5, hydrated for more than 3 yr at the time of examination. The resulting paste was of course very soft and had a consistency resembling talc stone. Microstructurally, it consisted almost entirely of bundled and intertwined, very fine fibers, some of them only about 50 A across, as shown in figure 20, and in figure 5a. Figure 5b also shows the ED pattern given by such fibers, which agrees with that of well-crystallized CSH(B) tobermorite.

The oldest pastes examined were two samples of w/c 0.70 and 0.35 which had been kept in sealed vials for nearly 10 yr. Figure 4a is a micrograph from the former sample containing, in addition to the C–A–H plate, some irregular, flaky gel clumps. The latter paste was very hard and difficult to grind. Both pastes were composed chiefly of dense gel aggregates of small flakes, with only minor amounts of fibrous phase visible.

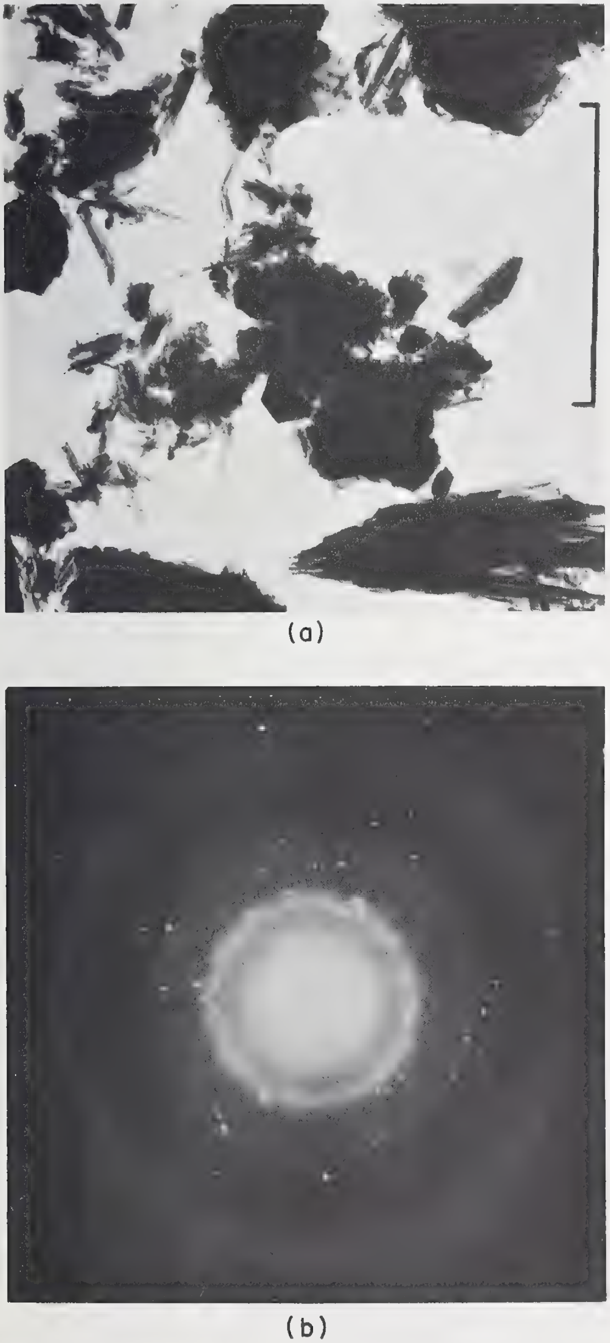
Observations on Pastes Cured at Elevated Temperatures

Hydrothermal curing of pastes for periods of short duration (less than a few days) at temperatures below about 150° C does not, as a rule, yield products of microstructural properties very different from those observed in pastes cured at normal temperatures. Kalousek and Prebus [30] show electron micrographs of the gel material in paste samples of cement and of a 60–40 percent cement-silica mixture, cured at 80 to 50° C for 15 hours. The complex XD pattern of the former product indicated, among other compounds, the formation of $C_2SH(B)$ (hillebrandite) and possibly some $C_2SH(A)$. The electron micrograph for this sample shows particles of various morphologic habits, tentatively identified by the authors, a few rod-like or tubular particles as hillebrandite, gel aggregates of partly fibrous appearance as C_2SH_2, thin plates as CH or $C_2SH(A)$. The cement-silica mixture consisted exclusively of irregular masses composed of small globules or plates.

The author examined a cement paste of w/c 0.46, autoclaved for 24 hours at 97° C and a pressure of about 700 kg per cm², then stored for about 7 years. No difference in appearance of the gel fragments in this paste and in those shown previously in this review could be detected.

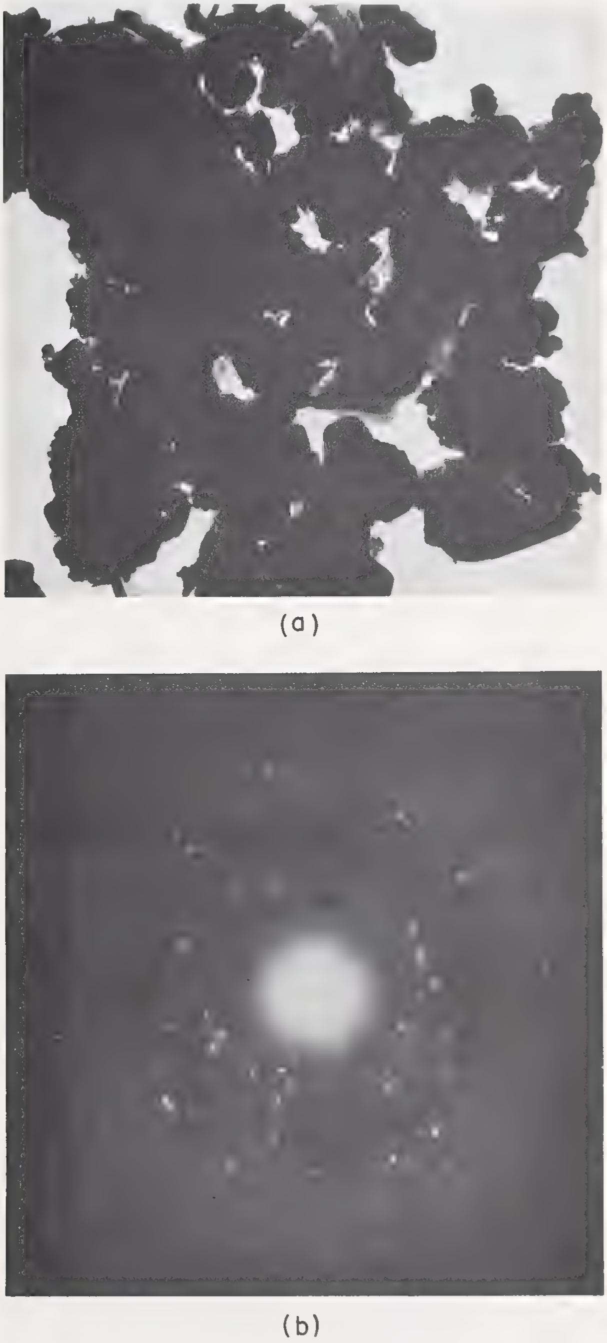
In another paste, cured at 177° C, but under otherwise equal conditions, the tendency to formation of fibrous structures was noticeable (fig. 21 a, b). The somewhat higher degree of crystallization is reflected in the increased intensities of the diffuse 2.7- to 3.1-A ring and the fiber reflection at 1.82 A. The spot reflections originate mainly from CH crystals, while C–A–H plates of the hexagonal C_4AH_{13} type could not be found in the specimen. Some lathlike or rodlike particles were identified, by means of their single-crystal ED patterns, as $C_3SH_{1.5}$.

A third paste examined, of Type I portland cement, w/c 0.40, had been autoclaved at 215° C for 24 hr, and then kept refrigerated for about 1 yr. The major part of this paste was found to be recrystallized, appearing as rather large, nontransparent crystal fragments together with CH crystal flakes (fig. 22 a, b). The ED pattern in figure 22 b shows a great number of irregularly distributed spots, considered to be the characteristic ED pattern from large and well-crystallized particles of a compound of low crystallographic symmetry. It is believed that the compound predominant in this paste is C_2SH(A). Other constituents, present in minor quantities, were bundles of long rods or laths, identified by ED as $C_3SH_{1.5}$, and aggregates of thin, rounded flakes (fig. 23 a, b) giving an ED pattern of spot rings, corresponding to the (hk) crossgrating reflections from a hexagonal unit cell of a_H=5.33 A. This compound can probably be identified as a synthetic clay (Al-Mg-silicate hydrate), formed from the cement constituents under the prevailing hydrothermal conditions.


(a)

(b)

FIGURE 21. *(a) Representative fibrous structure from a cement paste autoclaved 24 hr at 177 °C and a pressure of about 700 kg/cm², stored for about 7 yr. (b) Electron diffraction pattern of material shown in figure 21a.*


(a)

(b)

FIGURE 22. *(a) Crystal fragments believed to be* C_2SH(A), *together with* $Ca(OH)_2$ *flakes from Type I cement paste autoclaved at 215 °C for 24 hr and kept refrigerated for 1 yr. (b) Electron diffraction pattern of material shown in figure 22a.*

w/c=0.4.

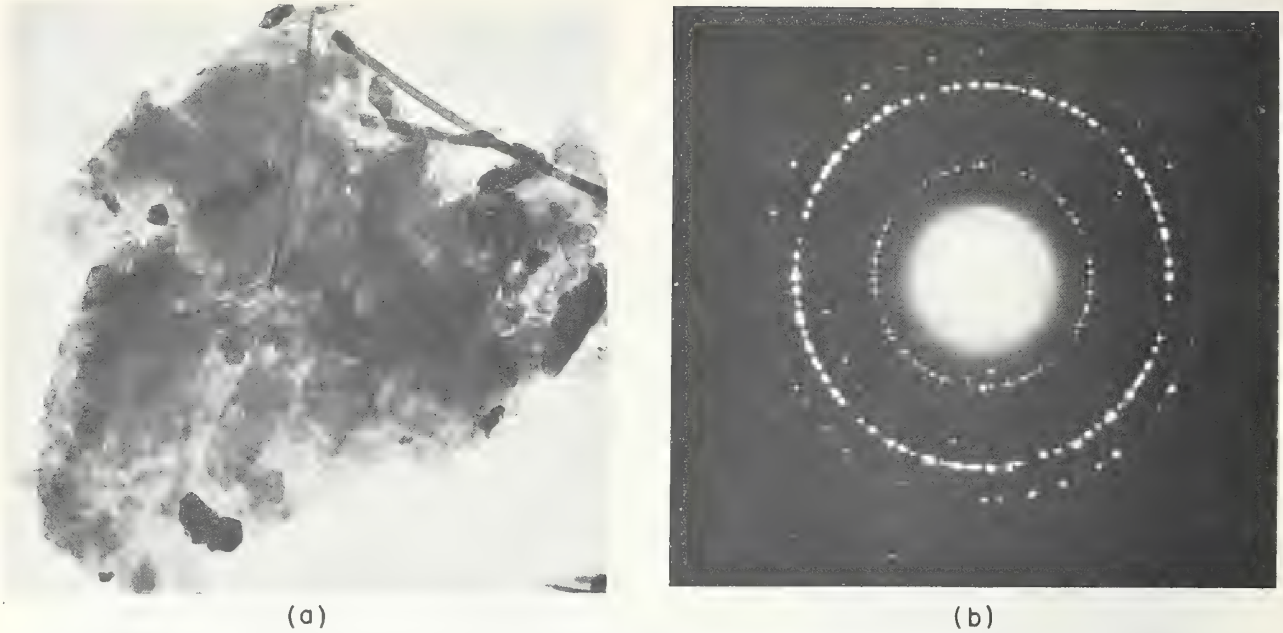

(a) (b)

FIGURE 23. *(a) Laths of* $C_3SH_{1.5}$ *and aggregates, probably synthetic clay* (Al-Mg-*silicate hydrate*), *present in minor quantities in Type I cement paste autoclaved at 215 °C for 24 hr and kept refrigerated for 1 yr.*

w/c=0.4.

Observations on Cement Paste by Replica Methods

A number of investigators in later years [93, 94, 95, 96, 97, 15] have reported electron-optical observations on thin replica films, of amorphous carbon or other materials, evaporated onto the surfaces of cement paste samples, and then stripped off or isolated by dissolution of the base material.

It is not surprising, considering the general lack of structure in cement gel particles as revealed in direct observations, that the replica studies have met with considerable difficulties of resolving the finer details of paste surfaces and of identifying various paste constituents from the appearance of their impressions in the replica film. In the opinion of the author, the employment of replica methods will be justified only if the results can be used to confirm or refute theories on the microstructural properties of hardened paste, based on data obtained in direct EM and ED observations of dispersed paste particles. As far as is known to the author, comparative EM studies of this kind, using both replication and direct observation, have not yet been attempted in any great extent. The particular branch of research on paste microstructure represented by EM replica techniques is in a state of rapid evolution. For this reason, it seems advisable, at the present time, to defer the discussion on this subject until it can be more clearly surveyed.

Experimental Data and Theories

The data presented here on the general morphologic character of ordinary cement pastes do not confirm the theories on paste structure advanced by Bernal [8] at the London Symposium. According to these theories, which were based on the information then available on the microstructural properties of C–S–H compounds (given, among many others, also by this author), the paste structure was visualized as a network of fibers which thickened in the course of hardening to a dense, feltlike mass, thus imparting a steadily increasing mechanical strength to the paste. According to the data given in this review, such a model can be applicable to special cases of cement hardening, but it seems that in ordinary pastes the fibrous structures are not formed in quantities large enough to make it safe to assume that a framework of fibrous structures could be mainly responsible for the strength and dimensional stability of the hardened paste.

It has been shown previously, that at least the various pastes examined by the author seem to have a nearly amorphous structure even after many years of curing at normal temperatures. This observation is contradictory to the views expressed by Rehbinder [42], and by Strelkov [13], in developing the theories originally formulated by Baikov on the course of paste hydration of cement. The opinion held by these authors is, briefly stated, that the first products of hydration formed during setting are precipitated as highly colloidal masses, and that these products are, in later stages of prolonged hardening, converted into crystalline products of continuously increasing degree of crystallization, forming in the end product a monolithic structure of intergrown crystals.

The statement that the fibrous constituents are unlikely to contribute much to the structural rigidity of certain types of pastes is also partly opposed to some views on cement hardening put forth tentatively in a recent report by the author [34]. These views were based on observations of hydration processes in cement slurries. However, taking all available evidence into account, it seems that the structures formed in the presence of an excess of liquid phase may be essentially different from those formed during setting of fresh paste of low w/c ratio, which material, as far as is known to the author, has not yet been studied with respect to microstructure.

A reconsideration of current ideas on paste microstructure is obviously needed, but the experimental material on the systematic influence of a number of different factors must be enlarged considerably, before any definite statements can be made.

Considerations on Microstructure in Relation to Physical Properties

It is evident that there are still a great number of problems concerning the microstructure of cement pastes remaining to be solved. Therefore, it would be very difficult, with the present set of data, to establish any functional relationship between microstructure and, e.g., mechanical strength, or other important physical properties such as creep under load, permeability, etc. However, it is not necessary to know in detail the molecular microstructures of various components of the cement gel, in order to develop, in mathematical terms, far-reaching theories on the general physics and the mechanical behavior of hydrogels, specifically cement paste, as is demonstrated by Powers and by L'Hermite, in their review papers of this Symposium. In view of the great variability of microstructures in different cement pastes, it seems that the only property remaining for a characterization of cement gel is the enormous specific surface area developed in the collapsing anhydride structures due to the penetration of water through them. The importance of the evolution of large surface areas in materials possessing hydraulic properties has been particularly stressed by Powers [98], and by Brunauer [99]. However, as is also emphasized by these authors, it is not only the development of surface, but also the nature of links formed between surfaces that determines the properties of cohesion and strength development in a paste. These links or bonds between surfaces may be largely of physical nature (absorption forces), possibly acting via intermediate layers of water molecules, but in view of the dimensional stability of hardened paste it seems that some parts of the interacting surfaces must be connected by means of strong chemical bonds (valence forces) formed in the process of a direct superposition and intergrowth of surface lattice structures. One of the objects for future cement research is to establish the nature of these links between surfaces, and the relative preponderance of different types of forces at various stages of hardening. The application of results obtained in structural studies on more well-crystallized materials may prove helpful in solving this problem.

Another question pertinent to the relationship between structure and mechanical strength, is whether the presence of any particular habit of the crystal elements (e.g., fibers) in a paste structure is more favorable for the development of strength than others. The evidence on this point given in the literature related to the subject is rather confusing. It has been reported that paste products consisting of, e.g., well-crystallized tobermorite plates show high strength, whereas pastes composed of fibers or crinkly foils may be poorly integrated. In other cases highly colloidal structures are observed in paste products of high mechanical strength. In still other cases a fibrous microstructure is associated with high strength, while a recrystallization of the structure leads to disintegration. Obviously such quantities as initial w/c ratio and porosity, curing and mixing conditions, etc., are also factors which influence the ultimate result as much as does the habits of gel particles. However, it would seem that in further research on the hardening of pastes the formulation of some fundamental theories on the influence of the shape and size of gel particle elements must also be included.

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Discussion

L. E. Copeland and Edith G. Schulz

Mr. Grudemo has presented a comprehensive review of the microstructure of hardened pastes, and in his review has pointed out certain areas where little or no work has yet been reported. He has concluded that "by far the largest part of the cement pastes examined consists of exceedingly ill-formed, colloidal products, in which it is sometimes difficult to discern any definite morphology". He further concludes that the data he has examined do not support the theory of paste structure proposed by Bernal [1][1] nor the views of Rehbinder [2] and Strelkov [3].

We have done some work in one of the areas of ignorance pointed out by Mr. Grudemo, the nature of the structures formed during the setting of cement pastes. The primary purpose of our work has been to see if we can learn more about the microstructure of hardened paste by following the development of structure in the paste from the time of the first addition of water to the cement until it is completely cured. We can now present some data on the morphology of fresh pastes.

Pastes were mixed with a water-cement ratio of 0.4 by weight using a procedure previously described [4], except that the pastes were mixed at atmospheric pressure and poured into covered plastic containers for curing. The treatment of the paste after it was mixed depended upon whether samples were to be taken before setting or after setting occurred. Curing times after mixing ranged from 1 min to 2 months.

Samples to be taken before setting occurred were sealed in air-tight containers and at the prescribed time the hydration process was stopped by placing the container in a freezing mixture of dry ice and alcohol. The frozen sample was then transferred to a vacuum desiccator and the ice was sublimed. If samples were to be taken after setting occurred excess water was added before the container was closed. At the prescribed time the sample was crushed and then dried in the vacuum desiccator.

Specimens for the electron microscope were prepared by grinding the dried samples in a synthetic-sapphire mortar, with pestle, suspending the ground material in 1,1,1-trichloroethane and subjecting the suspension to ultrasonic vibration for two min. A drop of the suspension was then placed on a carbon-covered parlodion film supported by a copper grid. The liquid was evaporated in a current of air free of carbon dioxide and the specimen was transferred immediately to the microscope.

Pastes were prepared from two commercial cements, lot Nos. 15754 and 15669, the phase compositions of which (by X-ray diffraction analysis) are:

	Cement lot No.	
	15754	15669
Alite, %	53.1	29.6
Belite, %	25.9	56.0
C_3A, %	6.9	1.0
Ferrite, %	9.7	5.8
Ferrite A/F	1.44	1.22

A series of electron micrographs of pastes made from each of the two cements has been selected to illustrate the development of structure in the colloidal masses of the paste. The micrograph for each time of curing was selected to represent the major products of hydration, so for the most part the series does not give a complete representation of hydration processes. For example, for the purpose of this work the formation of well-crystallized phases was of little interest, so no effort was made to include their development in this series. These same pastes will be reexamined later for this latter purpose.

Figure 1a is a micrograph of unhydrated cement 15754, 1b is a micrograph of cement 15669. The magnification is the same as that of the hydrated pastes which follow. The particles have smooth edges and sharp corners, and show little evidence of surface hydration. Hydration of the cement starts immediately upon contact with water. Within 1 min after adding water to the cement, small plates develop on the surfaces of the particles, and within 6 min small rodlike particles appear as the small plates increase in number. Some of the plates are hexagonal, others appear square. We shall try to identify these plates by electron diffraction in the future.

After 14 min, the hydrated layer is thick enough to cover the surfaces of the original grains of cement 15754 with the small, almost square plates, figure 2a. The hydration of cement 15669 proceeds more slowly, the surfaces of the cement grains being partially covered with a product having the same appearance as that described above, figure 2b. Acicular crystals of gypsum are present—probably formed during the quick freezing of the paste in the sample preparation. These crystals have a characteristic form and are easily recognized. Their identity was established by their electron diffraction pattern. The hexagonal plates are larger than those observed in paste samples taken at shorter times.

After 1 hr the layer of hydration products on the grains of cement 15754 no longer appears to be composed of small plates, figure 3a. The form of the particles cannot be distinguished. The appearance of the grains of cement 15669 hydrated for one hour is about the same as in pastes hydrated only 14 min, figure 3b.

Figure 4a is an electronmicrograph of a paste of cement 15754 after 2 hr of hydration. During the second hour, clusters of acicular particles have developed, along with the platelike particles. Clusters of acicular particles that do not seem to be associated with grains of cement are present.

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[1] Figures in brackets indicate the literature references at the end of this paper.

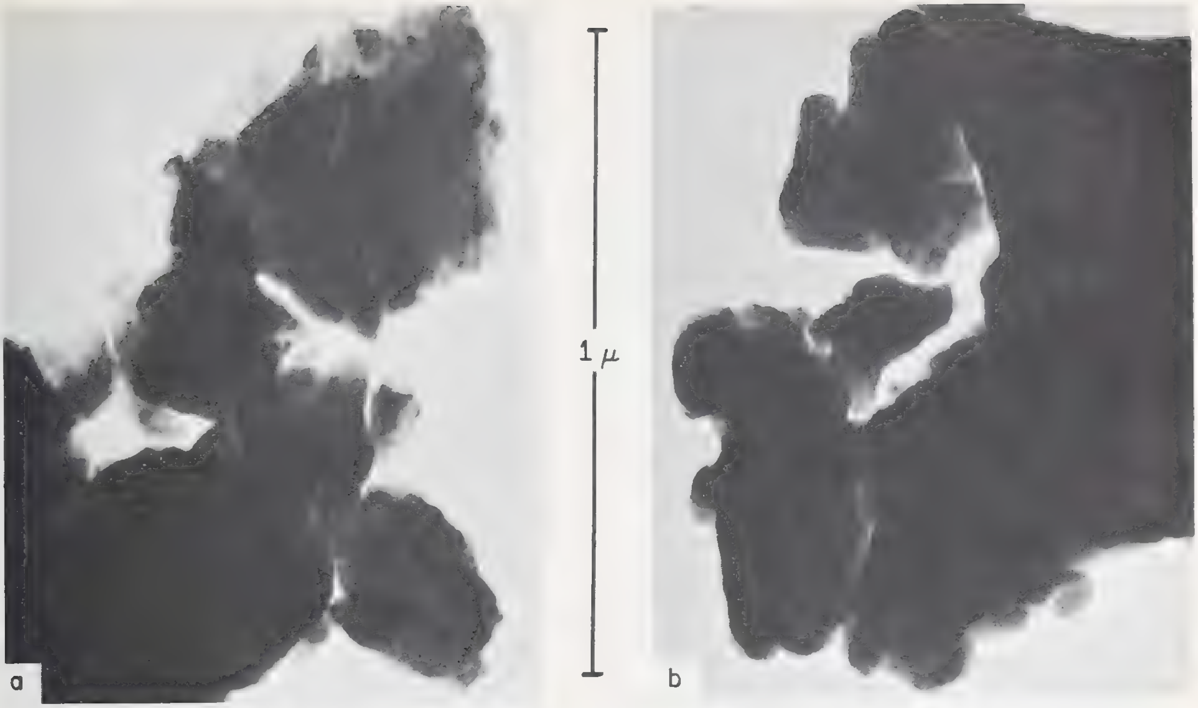

Figure 1. *Unhydrated cements.*

(a) Cement No. 15754; (b) Cement No. 15669.

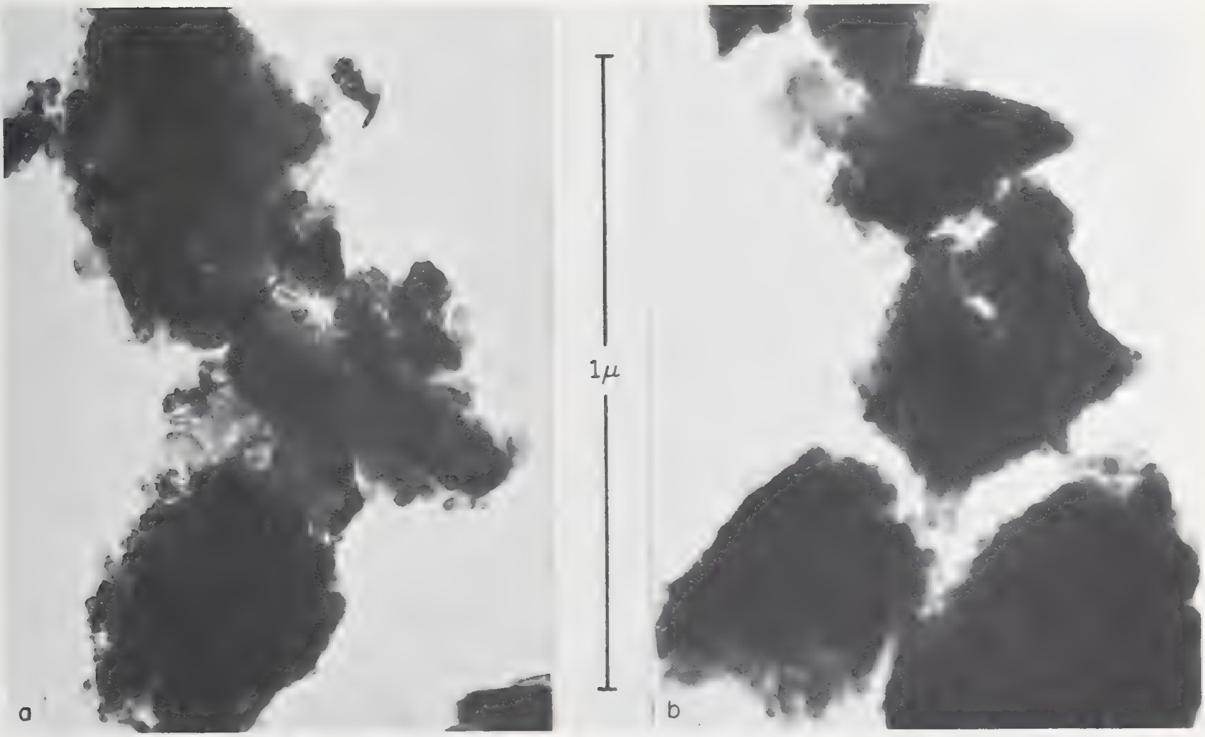

Figure 2. *Pastes hydrated 14 min.*

(a) Cement No. 15754; (b) Cement No. 15669.

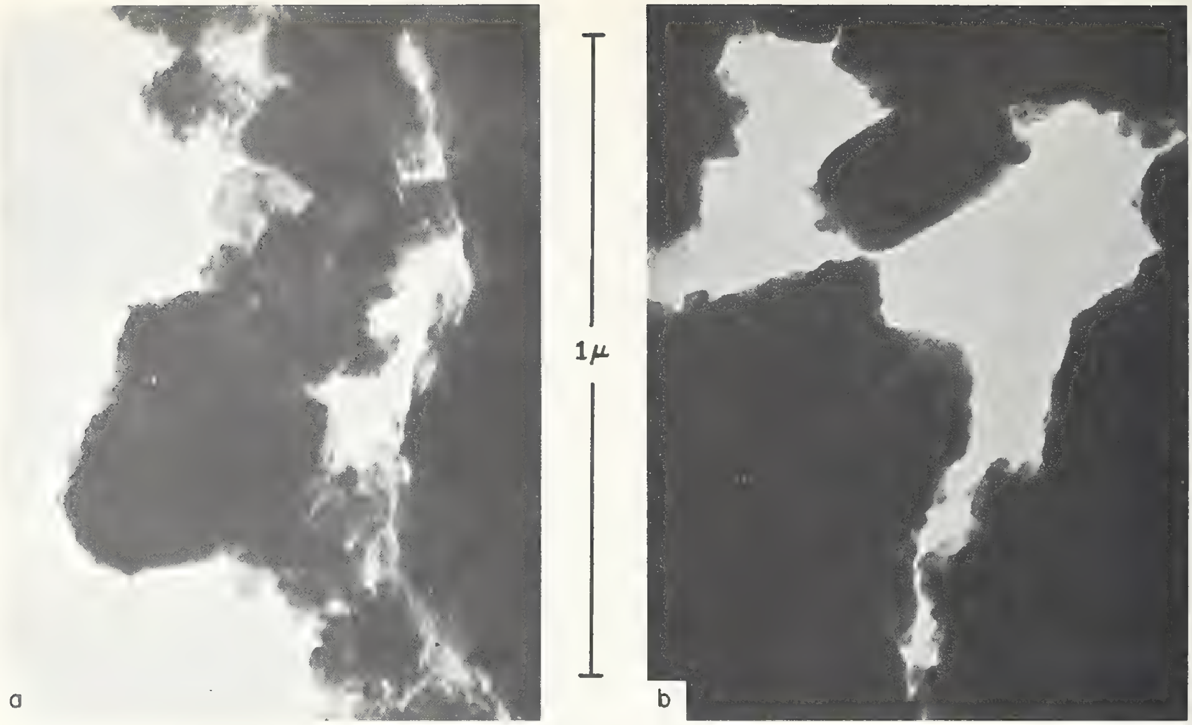

FIGURE 3. *Pastes hydrated 1 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

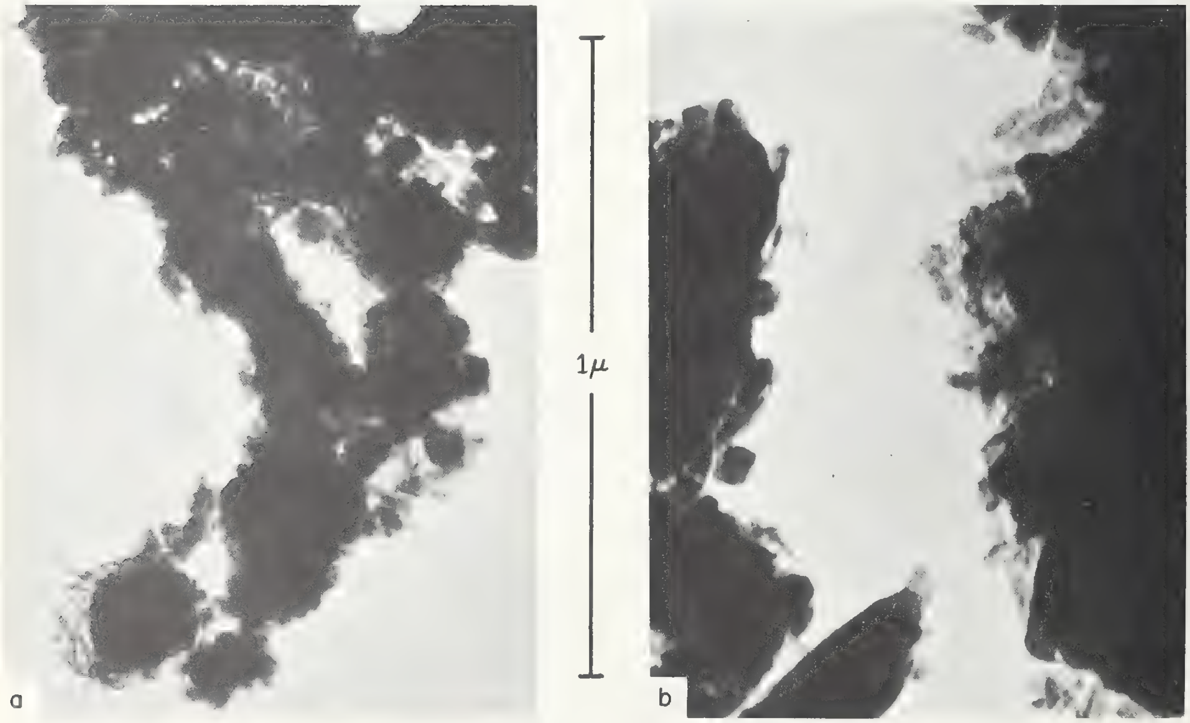

FIGURE 4. *Pastes hydrated 2 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

These may have precipitated from solution, or may have started on very small grains that are now completely covered or completely hydrated. Alternatively these clusters may have been broken from larger clusters formed on grains of cement.

No acicular products are present in the paste of 15669 after 2 hr of hydration. The small platelets continue to form on the surfaces of the grains, and the hexagonal plates are larger than before.

After 4 hr, the clusters in pastes of cement 15754 have grown larger, but the shape of some of the particles seems to have changed, in that some of the particles do not have as sharp points as others; the blunt particles are shaped more like laths, figure 5a. In pastes of cement 15669 clusters of acicular-shaped particles have appeared, and look much like the acicular particles present in pastes of 15754 after 2 hr hydration, figure 5b. However, in addition to the acicular particles one occasionally sees a particle embedded in the acicular clusters that looks very much like the rolled foils or tubes that are found in pastes of β-C_2S and C_3S. These rolled foils do not appear in pastes of cement 15754.

Figure 6a, from a specimen of paste made from cement 15754, shows that after 6 hr hydration the clusters have become larger, but the individual particles seem also to be getting broader. Acicular particles, lathlike particles, and broader platelike particles can be seen in the same cluster. The texture of surface is the same in all these particles, and makes them appear to be aggregates of exceedingly fine fibers. Figure 6b shows a small aggregate or a particle from a paste of cement 15669 cured 6 hr. The mass seems to be a single star-shaped particle, identical in appearance with the product formed in the hydration of cement 15754.

After 16 hr hydration the clusters of acicular particles have disappeared completely from the hydration products of cement 15754; a typical field is shown in figure 7a. The irregular aggregates appear to be formed by flat, thin plates which can be seen at thin edges of the aggregates. The surface texture of these plates is the same as that of the particles seen at earlier ages. The paste of 15669 hydrated for 16 hr, figure 7b, still shows clusters, but many lathlike particles and flakes are now evident. The outlines of larger lathlike or rodlike particles imbedded in the clusters can also be seen.

After 24 hr hydration, pastes of cement 15754 cannot be dispersed sufficiently to show individual particles. The thin edges of the irregularly shaped aggregates that one can see seem to be composed of thin plates or flakes. The surfaces of these plates are striated as if they were fibrous. Figure 8a shows one such aggregate with a pronounced fibrous appearance. The thin foil on the upper edge of the aggregate appears to be a continuous sheet even though striations are seen on it too. This micrograph is slightly underfocus, and the diffraction line around the particle indicates that the edge of the sheet is smooth—that the striations are not separated individual fibers. The appearance of this sheet is very much like that of crepe paper.

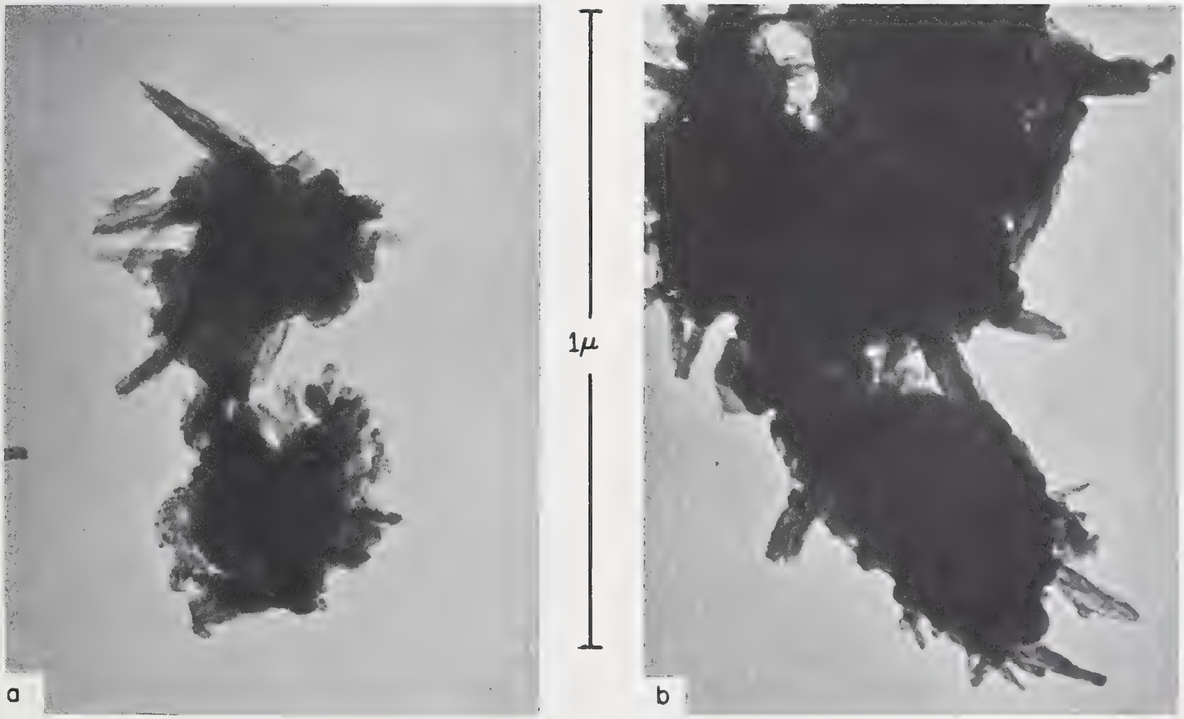

FIGURE 5. *Pastes hydrated 4 hr.*

(a) Cement No. 15754; (b) Cement No. 15669.

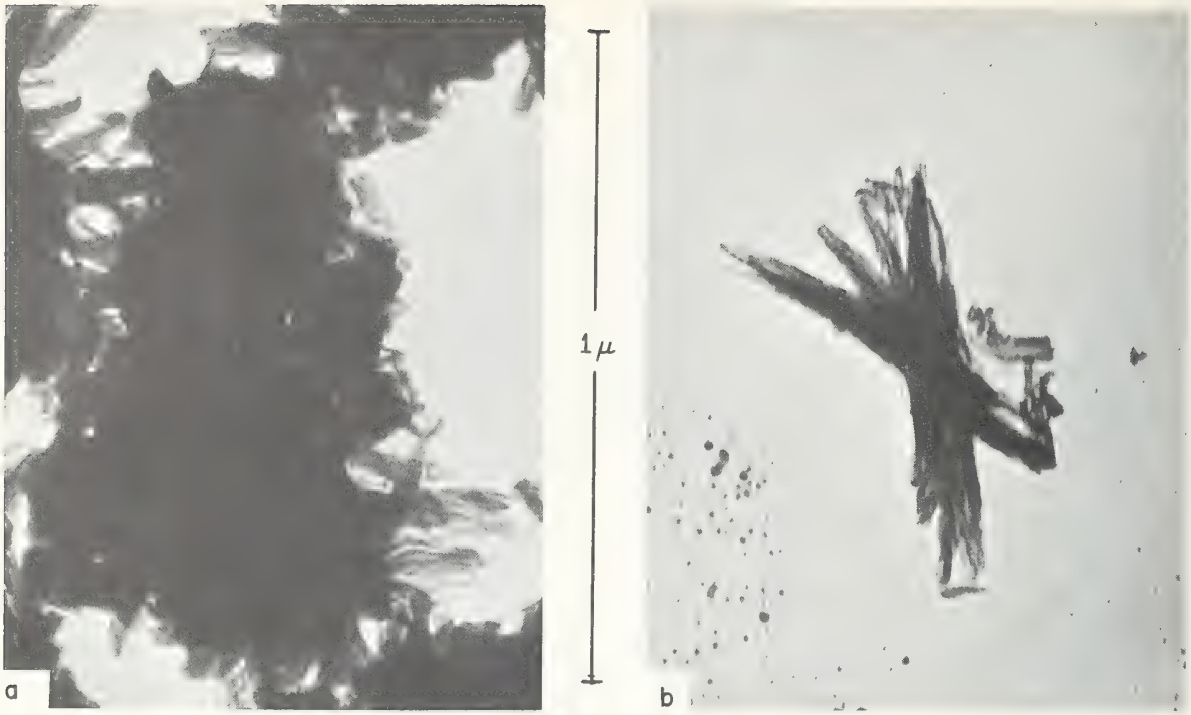

Figure 6. *Pastes hydrated 6 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

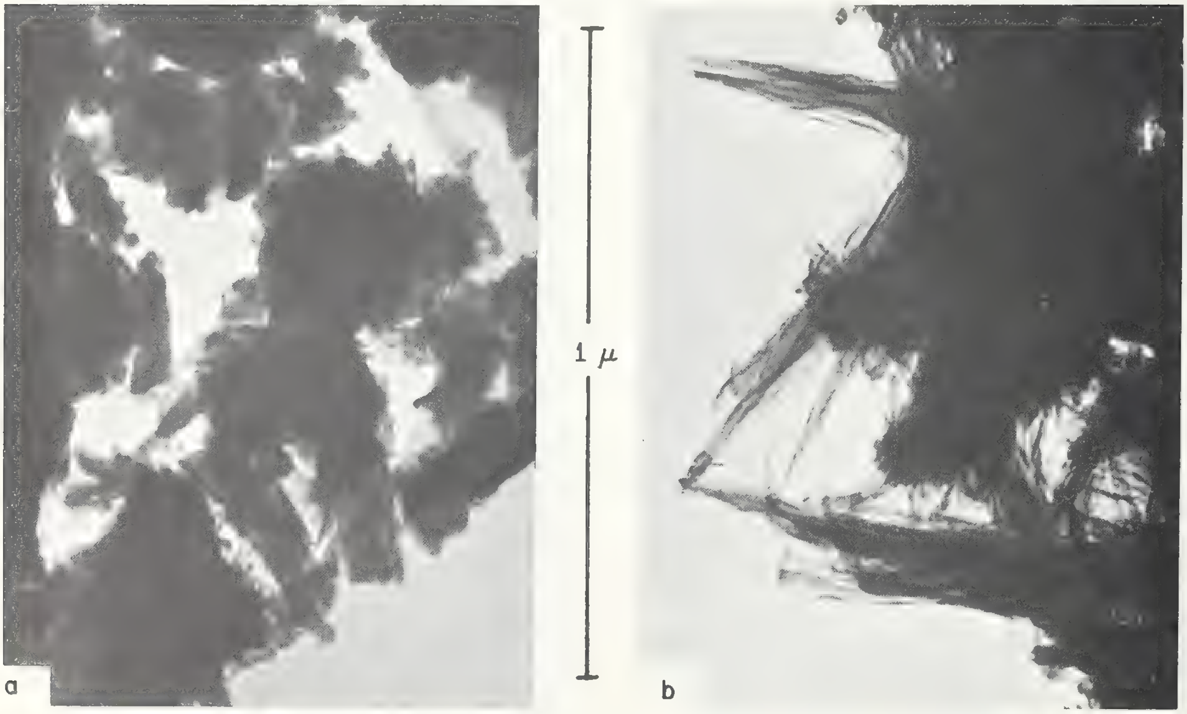

Figure 7. *Pastes hydrated 16 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

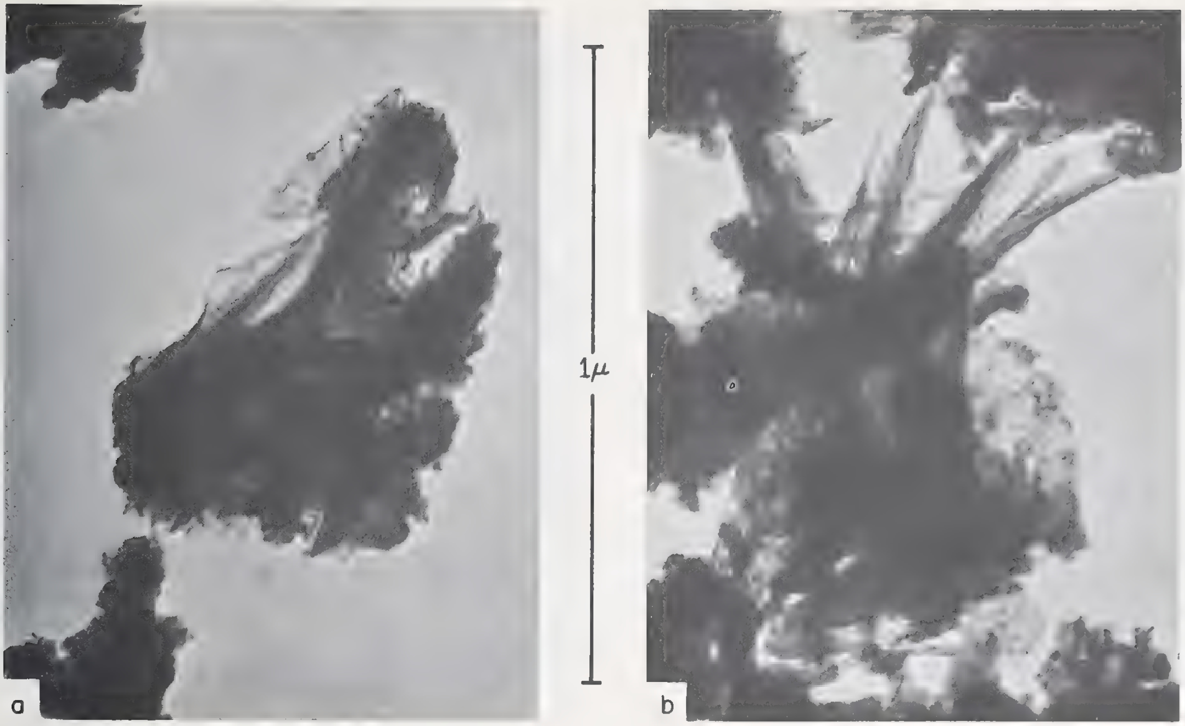

Figure 8. *Pastes hydrated 1 day.*

(a) Cement No. 15754; (b) Cement No. 15669.

The clusters of acicular and lathlike particles are still present in pastes of cement 15669 after 24 hr hydration. In the field shown, figure 8b, a cluster of acicular particles can be seen, in other fields particles similar to rolled sheets, so predominant in C_2S pastes, and sometimes thin sheets of flakes, can also be seen.

Figure 9a is a characteristic micrograph of a paste of cement 15754 hydrated for 2 days. The aggregates are too thick to show detail except at thin edges. Thin foils are visible with surface striations similar to those found in younger pastes. Occasionally one can find small thin, fragments like that appearing in this field. These have the same characteristic appearance of the hydration products seen in all these pastes.

The paste of cement 15669 after 2 days hydration is a mixture of rolled sheets or tubes and the irregular striated sheets seen in pastes of 15754. The particle at the right of the aggregate of particles shown in figure 9b has a thin sheet attached to it as if it were part of an outer layer of the roll that had been torn away. The surface texture of this sheet is similar to that of the striated sheets.

With longer curing times it becomes increasingly difficult to disperse the pastes sufficiently to see much detail in the structure. Pastes cured 7 days are shown in figure 10; figure 10a is a micrograph of paste from cement 15754, 10b that of a paste from 15669. Not much structure can seen be in 10a except that thin parts of the aggregate seem to be composed of sheets much like those seen in other micrographs. The striated sheets are more pronounced in 10b. A significant number of tubes or rolled sheets, were found in other fields.

No more details can be seen at 28 days hydration than can be seen in pastes hydrated several years. Figure 11a is a micrograph of a typical field from a paste of 15754. Thin regions of the aggregates appear very much like the product that can be seen in less well-hydrated pastes. Figure 11b is from a paste of 15669 cured 28 days The thin regions of aggregates again appear to be made of striated sheets. In other fields relatively large particles, shaped like rolled sheets seen in younger pastes, are embedded in the aggregates.

The effect of the difference in the rates of hydration of these two cements is evident in this work. The main characteristics of pastes of cement 15669 are about the same as those of pastes of cement 15754 at an earlier age. There is one important difference between the two sets: in pastes of cement 15669 many particles appear which are similar to those found in pastes of pure C_3S and β-C_2S, whereas these particles were not found in pastes made from cement 15754. It will be interesting to discover whether this difference is the result of the high belite content or low C_3A content of cement 15669.

The progress of hydration as seen in these micrographs suggests that the silicates in portland cement hydrate to form, at first, clusters of acicular particles. These clusters of acicular particles

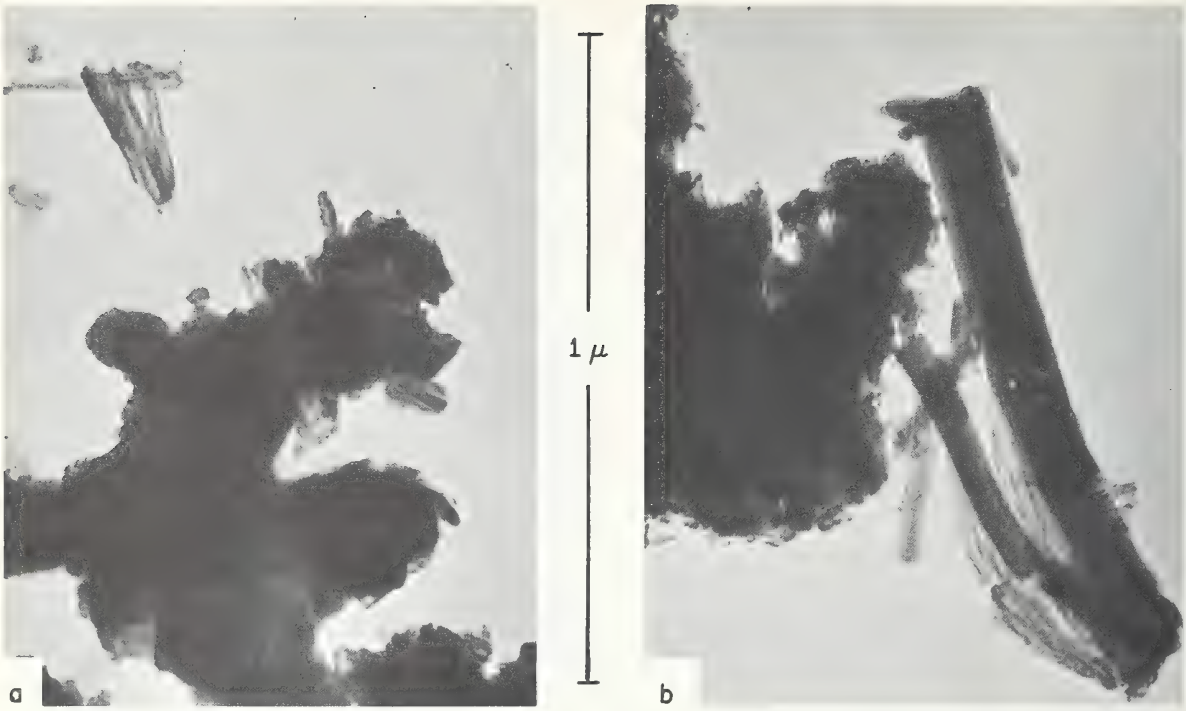

FIGURE 9. *Pastes hydrated 2 days.*
(a) Cement No. 15754; (b) Cement No. 15669.

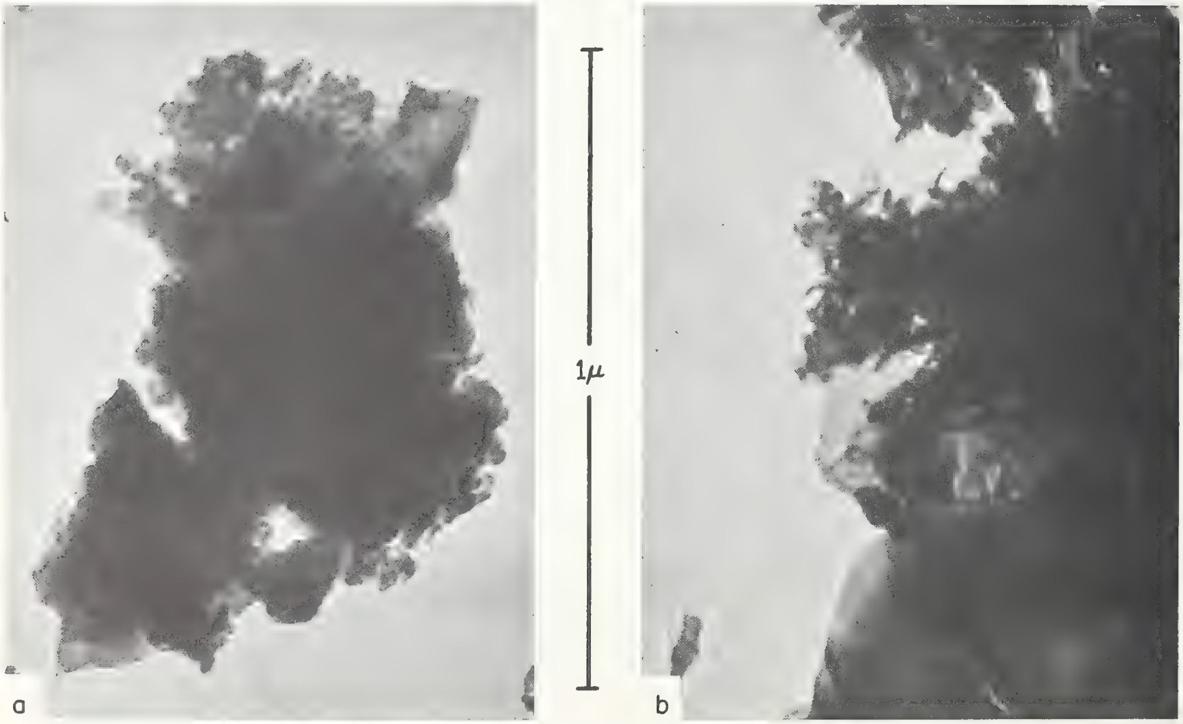

FIGURE 10. *Pastes hydrated 7 days.*
(a) Cement No. 15754; (b) Cement No. 15669.

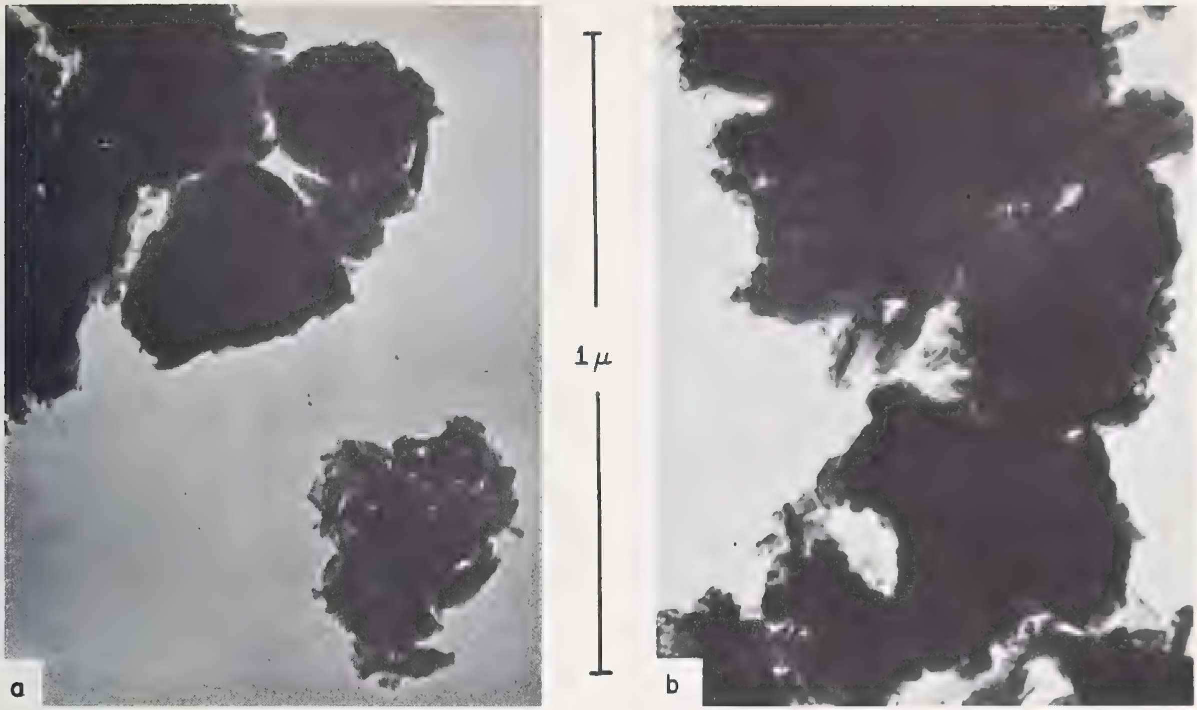

FIGURE 11. *Pastes hydrated 28 days.*
(a) Cement No. 15754; (b) Cement No. 15669.

are formed at about the time of the initial set of the paste. The clusters become larger and denser, and it seems logical to suppose that interlocking and growing together of the clusters of acicular particles causes final hardening. The absence of acicular particles and the presence of laths and sheets, or flakes, in the more hydrated pastes indicates that growth of the particle transverse to the axis of the needle formed initially must take place. The surface texture can be explained by strong orientation of the silica chains within the sheets.

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Discussion

Levi S. Brown

In discussion of the microstructure of hardened cement paste, there necessarily enters the particular concept of something happening in between the cement particles. The cement mix initially is a concentrated suspensoid of independent solid particles in water; shear resistance of the bulk mass is substantially zero. Within a time interval of minutes to hours the mass has become a single solid unit with very substantial shear resistance. The transformation results primarily from chemical reactions within the mass. It is known that the chemical reactions continue long after the arbitrary time defined as final set. It is known that cement still unhydrated is of common occurrence in good concretes after many years in service. In the light of these observations, the concept of something happening in between the grains becomes the central feature in investigations of the microstructure of hardened cement paste.

Being mechanical in nature, direct perception of the structure involves some sort of optical approach. The problem is especially elusive because (a) some 20 percent of the cement particles are individually in the size range of the wave length of light or below and (b) at the usable suspensoid concentrations the distances between the grains are of similar magnitude. Since this also is the limit of resolution by microscopy it follows that separate distinction of the fine particles, to say nothing of more specific identification, and the intervening spaces ranges into the impossible. The electron microscope of course notably extends the range, but at the disadvantage of interpretation of necessarily specialized subject preparation.

Cement particles actually are clinker particles. It is only in the size range of 5 to 7 μ and below that the particles tend to become monomineralic. Since 75 percent of the cement is above this size range, it follows that most of the cement particles, particularly the larger individuals, can be separately perceivable, as such, and further the clinker mineralogy recognized.

Observation of cement still unhydrated after many years in concrete of course means observation of the larger particles or, better, residuals of larger particles. The reason that these particles can persist for many years is, of course, in part because of their relatively large size. Far more importantly, however, it is because of very slow access of moisture. Significantly, such residuals are formed only in good concretes, that is, concretes that must be called good because of many years of satisfactory and unimpaired service in designed capacity.

In considering the microstructure of hardened cement paste, one may inquire as to the manner of long time hydration of these larger units. The question is easily subject to answer by direct visual microscopic observation of the initial and the altered material, by means of thin sections, powder mounts, or polished sections of the hardened cement paste or concrete. It is no trick at all to reveal the centers or cores of unhydrated clinker which, incidentally and by techniques well known, reveal also the clinker mineralogy. It is hardly more difficult to perceive in the altered material the initial boundary of the particle of clinker.

That is because the initial clinker structure is observed to be perfectly preserved. The initial structure, in brief, showed (a) angular crystals of C_3S and (b) nests of orbicular C_2S, together making up some 80 to 85 percent of the whole, enclosed within the (c) remaining 20 to 15 percent, which thereby is called "interstitial material", and which shows (d) itself to be made up usually of two components, one colorless (or dark, on polished sections) recognized as C_3A and one a dark brown (or bright, on polished sections) recognized as C_4AF. These, in some variation, are always perceivable. These initial minerals may be completely altered, yet these shapes, features, and mutual relations are seen to be perfectly preserved, and without evidence of mechanical distortion or volume change through the process of alteration.

The structure of the altered material is a perfect pseudomorph of the initial clinker. It is appropriate further to designate or to label the manner of alteration as pseudomorphous hydration. For this purpose, and for its significance, it is unnecessary to identify the secondary substances. That can be difficult. The best defined component is the interstitial material, which from location, isotropism, and refractive index can be identified as $C_3A \cdot 6H_2O$ or, with Fe_2O_3, as a hydrogarnet. The pseudomorphs of former C_3S or C_2S are variable, for reasons or under conditions not known.

It is the size of these larger particles that clearly defines this pseudomorphous hydration. Once recognized as such, it is relatively easy to recognize the remains of progressively smaller particles, though with progressively lesser clarity and security.

This manner of hydration holds, for the writer, yet more structural significance. As noted earlier, the mass of fresh concrete in the form comes into existence as a competent structural unit through a complex sequence of chemical reactions. The usefulness of concrete as constructional material rests on the fact that this profound and pervasive chemical alteration occurs without significant changes in imposed external dimensions. It is indicated thereby that the alteration must be pseudomorphous. That is to say that, if the cement particles in the mix ever lost significantly their mechanical resistance or rigidity, the external boundaries of the mass could not be expected to remain fixed.

It is appropriate, in conclusion, to offer a thought relating this pseudomorphous hydration to the more common concept of cementitious bond by something happening between the grains. The fluid in the cement mix, the continuous phase, initially is water. The cement minerals are unstable in contact with water. Initially the range of disequilibrium is extreme. Discussion of hydration processes usually centers about reactions through this disequilibrium period, for that generally is the period of set, with interest primarily in what happens in between the grains. The liquid in time, and perhaps not too long a time, approaches an equilibrium composition. Though never in equilibrium with the unhydrated cement minerals, the manner of interaction may be expected to be different from that of the earlier period, and likewise to be affected by the progressively lesser availability of the liquid.

Closure

Åke Grudemo

It is clear that the microstructure of hardened paste is conditioned by the processes taking place in the chemical reaction between the different cement components and water. A number of observations certainly indicate a high degree of interaction between the products of hydration of the various minerals in cement; nevertheless, the development of structure in cement paste is closely related to similar phenomena taking place in the hydration of the pure components.

In my paper, therefore, I found it necessary to summarize what is known about the microstructures of a number of materials of interest in cement hydration, and to give the essential features of the cement hydration chemistry in general, especially in what regards the microstructural aspects of this subject. Such reviews have been given more ably and much more in detail earlier in the Symposium.

Also Mr. Powers, of course, in his unique representation of the physical properties of cement paste, has had occasion to deal with a number of problems connected with microstructure.

In view of this I will confine myself to touching upon a few specific points of interest. It was a pleasant surprise to find that a comparison of the data given and the opinions expressed on microstructural problems in the independently written review papers seems to show that, at least in a broad sense, all of them tend to converge to give one and the same reasonably well-resolved picture of paste structure and properties. There are discrepancies and disagreement on some points, but in such cases the need of further research is clearly indicated.

What is then, in general, the picture of the paste microstructure that has emerged, especially out of electron microscope studies? First, it must be stated that the hardened paste does not consist of an integrated mass of uniform composition, but is a composite material containing several ingredients, some of them well crystallized, others with severely restricted or deformed crystal lattices. Most particles or aggregates of particles in cement paste of ordinary water-cement ratios fall in the latter category. In other words, the structural elements are exceedingly small, most of them in the truly colloidal size range, and of ill-defined outer shape. The habit of thin plates predominates, but the tendency to fibrous growth is quite noticeable in most pastes, and seems to be promoted by a high water-cement ratio, by steamcuring at not too high temperatures, and by a high C_3S content in the cement.

The phase now described is generally recognized to be mainly a calcium silicate hydrate, of a C/S ratio somewhere between 1.5 and 2, and structurally related to tobermorite. This is clearly brought out in electron microscopy studies of C_3S and C_2S pastes, which are somewhat better crystallized, at least partly, than the C–S–H component of cement pastes. In the pure pastes, fibrous or needlelike particles are commonly found, which in electron diffraction diagrams show a series of diffuse spot patterns, of a modified single-crystal type, clearly identifying these particles as being structurally intermediate between a disorganized C–S–H gel, and well-crystallized tobermorite. Similar particles are seen occasionally also in ordinary cement pastes. In special cases of paste hydration, such as in high-porosity pastes with finely ground cement, there may be an extensive formation of well-crystallized fibers of tobermorite.

The generally lower degree of crystallinity of cement gel particles can probably be ascribed to structural disturbances caused by the incorporation of aluminum ions in the lattice, probably substituting for silicon in tetrahedral positions, as was shown by Kalousek, in the case of well-crystallized, platy tobermorite, where a diminution of crystal size was observed. In this connection we must also consider the phenomenon of increased fibrosity and more regular crystallization of tobermorite (G) observed in the vicinity of C–A–H plates of hexagonal crystal symmetry, slowly crystallizing out in pastes. The segregation of such particles may be associated with a transport of aluminum ions from the C–S–H gel phase to the C–A–H plates, causing the lattice disturbances in C–S–H to disappear. However, if such a process occurs, it is still only a local, diffusion-controlled reaction, and probably leaves most of the gel unaffected.

Similar slow processes of segregation may occur in hardened pastes in the case of the crystallization of large CH plates. It can be imagined that the material required is taken from the residue of amorphous material of composition CH, the existence of which has been evidenced in studies made by Brunauer and his coworkers. In any case, the hardened paste is a remarkably stable system, and the possibly occurring processes of recrystallization certainly proceed at a very slow speed, after the paste has reached a certain age.

Concerning the question of the lattice structure of tobermorite gel, and its modification with increasing C/S ratio up to 1.5 or 2, I would like to draw your attention to a number of conflicting ideas. Gard, Howison, and Taylor, as well as myself, describe the change taking place as probably caused by the gradual stripping off of metasilicate chains from the tobermorite layer, resulting ultimately in unsymmetrical 1:1 layer units instead of the symmetric 2:1 layers. Alternatively, Buckle and Taylor advanced the theory of the formation, in C_3S pastes, of an inhomogeneous C–S–H material, in which there is a short-range variation of structure between the extremes given by low-lime tobermorite, and calcium hydroxide. Kurczyk and Schwiete give a model of high-lime tobermorite consisting of low-lime tobermorite layers alternating with complete layers of CH, of distorted or disorganized structures. Brunauer and Greenberg, finally, conclude from certain rate-of-solution experiments, that the incorporation of excessive amounts of lime in the tobermorite gel structure is accompanied by a gradual breaking up and depolymerization of the metasilicate chains. They arrive at a silicate chain model resembling the one given by Bernal at the London Symposium, in which an important feature is the presence of hydrogen bonds connecting silica groups in the direction of the chain. Clearly, the question of the tobermorite gel structure cannot be solved without much further work.

In this connection, I would like to point out another interesting observation made by Gard, Howison, and Taylor. They noticed that unimolecular layers of well-crystallized tobermorite sometimes overlap, not with their fiber axes in parallel, but rotated at approximately hexagonal angles to each other. Such a process of overlapping might account for the appearance, in less well-crystallized tobemorite gels, of particles of the habit of small plates, rather than fibrous or needlelike crystals.

The ultimate paste structure is obviously conditioned by the prehistory of the material, that is, the course of development of the microstructure during the early period of cement hydration, in which a number of processes involving rearrangement of the structural elements proceed simultaneously at comparatively high rates of speed. There are many indications, among others some derived from electron microscope studies of cement slurries, that the development of the hydrated phases is not a straightforward process, as perhaps the continuously and uniformly increasing stiffness and strength of the cement paste might indicate. Transient phases may develop, only to disappear at later stages. The balance in the solution phase between the amounts of the more easily hydratable compounds of cement clinker, together with the effects of sulfate and other admixtures, are obviously decisive factors in the development of microstructures in setting pastes. However, the relationships involved here have not yet been studied in a very systematic way with respect to microstructure, but remain as very important problems for future research.

A valuable contribution to our knowledge of the internal microstructure at different early stages of paste hydration was presented by Dr. Copeland and Mrs. Schulz. Some observations that I have made recently on similar materials are in very good agreement with those made by Copeland and Schulz. It also seems to me that in future work on the development of colloidal hydrate structures, attempts should be made to correlate data on microstructure with the observed rheological properties of different pastes, as described in the paper by Dr. Ish-Shalom and Dr. Greenberg.

It can be stated, as a conclusion, that in applying our knowledge of paste structure in the study of the mechanical properties of cement paste, we must concern ourselves with the formation and spatial distribution of different types of bonds between the surfaces of gel particles. To the experimenting chemist, at least, it seems to be an extremely difficult problem to treat theoretically the relationship between bond formation in a colloidal system of particles, and the mechanical behavior of construction elements.

Paper V–3. Volume Changes of Concrete*

Robert G. L'Hermite

Synopsis

The purpose of the present report is to give an up-to-date account of the present state of knowledge on the deformation of concrete.

The following phenomena have been examined: hygrometric, thermal, chemical, and dynamic phenomena (action of forces) in relation to the nature of cement, of aggregates, and the composition of the concrete.

A certain number of questions remain unanswered, in connection with which certain hypotheses have been put forward:

Is the internal mechanism of shrinkage a hydroconstrictive phenomenon due to an equilibrium between the liquid phase and the vapor phase, or does it arise from the crystalline phase in the form of physically bound layers of water?

Does creep continue indefinitely though at a continuously reduced rate or is creep a phenomenon of limited amplitude?

Are creep and shrinkage two aspects of a single phenomenon or are they two distinct phenomena linked by correlation?

What is the explanation of creep on the scale of the structure?

Is the phenomenon of the resumption of creep in water after a pseudostabilization under dry conditions linked to the movement of the water or to the resumption of hydration of the cement?

The report has appended to it a specially prepared bibliography containing 230 references.

Résumé

Ce rapport constitue un document de mise à jour quant aux connaissances actuelles sur la déformation du béton.

Ont été évoqués les phénomènes suivants : hygrométriques, thermiques, chimiques et dynamiques (action des forces) en relation avec la nature du ciment, celle des agrégats et la composition du béton.

Un certain nombre de questions restent posées à propos desquelles ont été émises certaines hypothèses :

Le mécanisme interne du retrait est-il un phénomène hydro-constrictif dû à un équilibre entre la phase liquide et la phase vapeur ou prend-il son siège dans la phase cristalline sous forme de couches d'eau liées physiquement?

Le fluage se poursuit-il indéfiniment quoiqu'à vitesse continuellement réduite ou le fluage est-il un phénomène d'amplitude limitée?

Le fluage et le retrait sont-ils deux aspects d'un même phénomène ou sont-ils deux phénomènes distincts liés par corrélation?

Quelle est l'explication du fluage à l'échelle de la structure?

Le phénomène de reprise du fluage à l'eau après une pseudo-stabilisation à sec est-il lié au mouvement de l'eau ou à la reprise de l'hydratation du ciment?

Le rapport est suivi d'une bibliographie spécialement réunie et qui contient 230 références.

Zusammenfassung

Dieses Referat gibt den heutigen Standpunkt der Kenntnisse was die Verformung des Betons anbetrifft.

Die folgenden Vorgänge wurden behandelt : Feuchtigkeitsgehalt, thermisches, chemisches und dynamisches Verhalten (Wirkung der verschiedenen Kräften) in Verbindung mit der Beschaffenheit des Betons.

Eine gewisse Anzahl Fragen stehen noch offen und folgende Vermutungen wurden angestellt:

Ist der innere Vorgang des Schwindens eine wasser-zusammenziehende Erscheinung abhängig von dem Gleichgewicht der Wasser- und der Dampfphase oder befindet sich der Sitz dieses Vorganges in der Kristallphase in der Form von physikalisch gebundenen Wasserschichten?

Ist das Kriechen ein zeitlich unbegränzter Vorgang obwohl mit beständig verminderter Geschwindigkeit oder ist das Kriechen eine begränzte Grösse?

Sind Kriechen und Schwinden die beiden Erscheinungen eines selben Vorganges oder sind diese beiden Vorgänge verschieden und in Wechselbeziehung stehend?

Welches ist die Erklärung des Kriechen was die Struktur anbetrifft?

Hängt das Wiedereinsetzen des Kriechen unter Einfluss von Wasser nach einer pseudo-Stabilisierung unter trockenen Verhältnisse mit der Wasserbewegung zusammen oder mit der, wieder in Gang tretender Wasseraufnahme des Zements?

Dem Referat folgt eine speziell zusammengestellte Bibliographie mit 230 Referenzen.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Laboratories du Bâtiment et des Travaux Publics, Paris, France. (This paper was presented at the Symposium by H. Woods).

Introduction

Variations in the volume of concrete may be due to a variety of factors: hygrometric, produced by a variation in water content; thermal, produced by temperature changes; chemical, produced by variations in structure; dynamic, produced by applied loads.

In general, the effects to which these factors give rise are not cumulative or commutative, yet while they may be studied separately, their combinations have a complex aspect that is as yet little known.

In a necessarily limited account it is not possible to enter deeply into details, and we shall do no more than examine the state of present knowledge, attempt to make a synthesis, and indicate the areas still to be explored. A broad bibliography will enable readers to discover the elements requiring further study.

Thermohygrometric Variations in the Volume of Young Concrete (First Shrinkage)

The setting and hardening of a hydraulic binder is accompanied by a variation in its apparent volume. When a pure cement paste is cured from the time of its mixing in an excess of water in the form of a de-aired slurry, the whole undergoes a contraction in absolute volume. This phenomenon has been brought out by Le Châtelier who has shown that the volume of hydrates is always less than the sum of the absolute volumes of the anhydrous components and the water. At 7 days this contraction is of the order of 12 percent of the volume of anhydrous portland cement [1, 2][1]. It is higher for aluminous cement. While the absolute volume diminishes, however, the apparent volume of the paste cured in the presence of an excess of water increases in a continuous manner. During the first hours this swelling is augmented by a thermal dilatation due to the release of heat produced by the chemical reaction of setting.

In air, cement and concrete begin to show a shrinkage before setting begins. Since the binder does not yet have any other than a capillary cohesion, this shrinkage can give rise to cracks. Several optical methods have been used to make such measurements [3, 4]. The results of tests show that during the first hours shrinkage depends on the conditions affecting evaporation of the mix water: humidity, temperature, rate of flow of air, absolute volume of test piece. Rapid shrinkage generally manifests itself between 1 and 2 hr, often preceded by a slight swelling. After 6 to 10 hr, it slows down to assume the habitual course of hardened cement.

On slabs of pure cement paste 2 cm thick the influence of the speed of ventilation of air at 50 percent relative humidity, temperature 20 °C, gave the following shrinkage results for a portland cement, after 8 hr: without forced ventilation, $1{,}700\times10^{-6}$; ventilation at 0.6 m/s, $6{,}000\times10^{-6}$; ventilation at 1 m/s, $7{,}300\times10^{-6}$. R. Dutron's tests confirm these results and indicate a shrinkage of $14{,}000\times10^{-6}$ for ventilation speeds of 7 to 8 m/sec of air at 20 °C. For air at 100 °C he obtained figures of the order of $19{,}000\times10^{-6}$ [5]. A 7-cm layer of pure paste without forced ventilation gave at the same time 850×10^{-6}. These figures, which differ by an order of magnitude, show the importance of ventilation.

The nature of the cement is of importance, since with a speed of aeration of 1 m/sec, blast-furnace cement gives $4{,}100\times10^{-6}$, portland cement $7{,}300\times10^{-6}$ supersulfated cement $10{,}000\times10^{-6}$.

The shrinkage of concrete at an early age is less than that of pure paste. Figure 1 shows the appearance of the shrinkage curves and indicates that shrinkage is increased with the proportioning, Rilem-Cembureau mortar having a cement content halfway between mortar and pure paste.

For a series of concretes, the first shrinkage varied between 800×10^{-6} with a content of 200 kg/m^3, $1{,}600\times10^{-6}$ with a content of 350 kg/m^3, and $2{,}300\times10^{-6}$ with a content of 500 kg/m^3. The quantity of mix water has an influence on concretes, shrinkage at an early age increases with the water/cement ratio, passes through a maximum, and then diminishes.

For a concrete proportioned at 350 kg/m^3, the following results were obtained:

w/c	0.45	0.50	0.55	0.60
shrinkage$\times10^6$	1,000	1,550	1,600	1,350

The influence of plasticizers is marked, the addition of these having the effect of increasing the initial shrinkage.

The initial shrinkage can be explained only in part by the loss of water. A shrinkage is in fact equally to be observed in the absence of any evaporation, which appears to be due to a settling by gravity and the action of capillary forces [6, 7]. in any case, the first cause is dominant and, by the time the surface becomes dry, the loss in volume is of the order of magnitude of the loss of water up to the time when the grains enter into contact and a structure is established; then the law of shrinkage assumes a different form. It is observed that the bleeding of the water in part opposes the first shrinkage by producing a wet surface which prevents internal evaporation.

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[1] Figures in brackets indicate the literature references at the end of this paper.

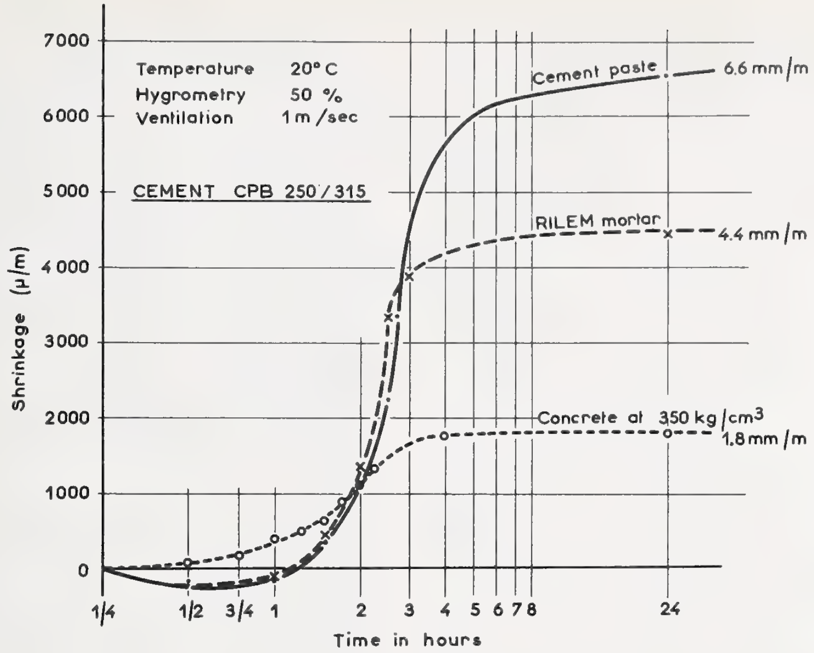

FIGURE 1. *Shrinkage from 0 to 24 hr after placing.*

This first shrinkage can have awkward consequences for building, for the decrease in dimensions contrasts with a reaction of the adjoining parts composed either of the parts of the volume having lost less water, or by the support. There may result cracks on the surface or in depth [8]. A familiar illustration is the cracking of the pavement of concrete roads, the cracking of plaster, etc. The behavior of cements, however, is as we have seen rather different, depending on their nature, that of concretes or mortars depending on their proportions, their water/cement ratio, and the addition of products like plasticizers. This is why cracking tests have been devised. One of these consists in applying a 2-cm coating to the surface of a concrete beam, and ventilating it at a speed of 1 m/sec with air at 50 percent relative humidity. The mortar having 1:1 portland cement cracks after 20 min, 1:2 mortar cracks after 1 hr 10 min, and 1:2.5 mortar does not crack. The adding of a plasticizer accelerates the cracking, but the corresponding risk appears only in the first hours; after setting this risk diminishes. For concrete, the test consists in grinding a flat test piece held in place at its broadened ends in fixed heads. The first cracking can be counteracted by preventing or slowing down the evaporation of the water either by protective membranes (curing compounds), or by artificially keeping the surfaces moist [9, 10].

Thermohygrometric Variations in the Volume of Concrete in the Course of Hardening

This dimensional variation is usually called shrinkage. It constitutes a different phenomenon from that dealt with in the preceding paragraph in that it applies to a material that is solid, even though porous, having a structure that is continuous while it is at the same time in evolution.

We may note that the term shrinkage generally includes swelling due to physical and chemical causes independent of the hydroconstrictive movement. We shall therefore speak first of this phenomenon.

Hygrometric Swelling of Cements and Concretes

A cement cured uninterruptedly in water from the time of its molding swells. The initial measurement being made at 24 hr after mixing, this swelling continues at a reduced rate. For a portland cement paste we found, for example, the following linear elongations [7]: at 100 days, $1{,}300\times10^{-6}$; at 1,000 days, $2{,}000\times10^{-6}$; and at 2,000 days, $2{,}200\times10^{-6}$.

Generally speaking, cements of this kind have at 3 yr a linear swelling of from 0.6 to 1.5 percent. According to Dutron [11] the quantity is thus quite variable. An increase in weight accompanies the swelling which occurs with an absorption of water greater than that which would correspond to the increase in volume. This result therefore means that there is in fact contraction in the liquid-solid combination at the same time as an increase in the apparent volume. The increase in weight after curing in distilled water, for portland cements, is between 3 and 5 percent, from 1 to 1,000 days, which would correspond to an increase in voids of 8 to 10 percent of the volume of the sample, 12 to 16 percent of the volume of the anhydrous cement; this figure corresponds to that given by Le Châtelier's method. It thus seems that swelling is indeed a phenomenon of chemical origin that accompanies hardening.

The swelling of concrete in water is much less than that of a neat paste. For a concrete proportioned at 300 kg/m^3 the linear expansion at 1,000 days is 100 to 120×10^{-6}, with an increase in weight of 1 percent at 1,000 days. The mortars have an expansion of 150 to 300×10^{-6} for a cement content of 500 kg/m^3. Dutron [11] has studied the influence of the nature of the cement and demonstrated a greater expansion of aluminous cement and a lesser expansion of slag cement (at 275 days): aluminous cement, 300×10^{-6}; rapid-hardening portland, 240×10^{-6}; ordinary portland, 230×10^{-6}; slag cement, 160×10^{-6}. Mixes of slag and portland cements, however, may give an expansion greater than that of portland cement alone. These differences are greatly reduced in the case of concretes. The law of swelling in terms of time is difficult to define precisely. At the outset it often appears to have the form $\Delta = Q \log t$ where Δ is the linear expansion, t the time, and Q a constant. It should not be deduced from this equation, however, that cement swells indefinitely, but if there is a limit, Δ_m, the latter cannot be derived from tests even extended over several years. Tests of paste carried out over 6 yr have not reached a stable value, the annual variations being of the order of magnitude of the experimental errors. For concrete, moreover, the swelling phenomenon stabilizes much more rapidly than for neat cement paste. It practically stops between 6 months and 1 yr, although the increase in weight appears to persist over a longer period. It is to be noted that at the beginning of hardening a shrinkage under water may be observed [11], but this varies with the dimensions of the test piece, the proportions, and the grain size. It is very visible on neat pastes, attenuated on mortars, and disappears for concretes except in the case of aluminous cements. The shrinkage appears to be due to the internal desiccation brought about by such rapid hydration that the supply of outside water cannot compensate because of the impermeability of the mix. Attempts made on very fine sheets of cement appear to tend to make this phenomenon disappear, and it might be considered to be an "effect of volume".

Chemical Expansion of Cements and Concretes

Although the hygrometric swelling may be explained as having a chemical origin, it is possible to separate the factors due to the normal hydration from those due to another influence either in the composition itself of the curing water or in that of the product itself aside from its fundamental components, the silicates and aluminates. The swelling of ordinary portland cement after about 2 yr is three times greater in sea water than in distilled water. A portland slag cement swells three times less than a portland in a 5 percent magnesium sulfate solution.

Is such swelling bound to lead to disaggregation? Not if it becomes stabilized below a limit within which the mechanical properties are not affected. It is possible to know this fact through the measurement of vibratory modulus of elasticity which shows a diminution at the beginning of disaggregation.

It seems that disaggregation is due to a discontinuous swelling in the volume on a microscopic or macroscopic scale. The former case is, for example, one in which the surface swells much more than the interior; it is subjected to considerable compression and disaggregation through flaking. The latter case is brought about when there are nuclei of expansion within the volume, discontinuous and distributed microscopic nuclei. Such is the case where there is free lime and also where there is an attack by lime sulfate. There is a combination of this salt with the lime aluminate in the cement and a formation of sulfoaluminate. If the sulfate combines with the aluminate without previous dissolution of the latter, swelling results, and regular clefts are formed in the mortar [2] due to the presence of expansion nuclei.

A thoroughgoing study of swelling in terms of composition has been made by R. H. Bogue [12] who draws a number of conclusions, including the following: expansion increases with the free lime content, the effect of which is especially appreciable between one month and three months; and it increases with the magnesia content, but the effect is much slower. The presence of magnesia makes cements more sensitive to the action of sulfates [13]. Goggi [14] indicates that expansion increases with the content of aluminate in the crystalline form.

Another highly important contribution is that of L. Blondiau [15] who used mainly the autoclave test advocated by the A.S.T.M. for accelerating the phenomenon, and, like R. H. Bogue, he deduces therefrom a justification for this method. He indicates in particular that the addition of pozzolanic materials to the slag markedly diminishes the swelling.

The boiling-water test long advocated by Le Châtelier has the advantage of bringing out very rapidly the presence of free lime and free magnesia, provided the treatment is prolonged for at least 5 hours.

Finally an expansion may be produced by the reaction between the cement and the aggregates. We merely call attention to it here for it is dealt with elsewhere in this symposium (N. Plum et al.). It may likewise be due to mixes of cements reacting chemically [16]. A mix of portland cement and aluminous cement gives, for 30 percent of the former and 70 percent of the latter, a swelling in water at the end of a year three times the average of those of the two components.

Thermal Dilation of the Concrete

Thermal dilation is generally expressed in the form of a coefficient of expansion. In the case of concrete, this coefficient is a function of numerous factors such as composition, age, water content, temperature, etc.

Tests on neat paste [17] show a very marked influence of the curing hygrometry preceding the test according to the age of the concrete at the moment when it is carried out. At 20 days for example the coefficient in microns per meter and per degree, $\frac{\Delta l}{lt}\times 10^6$, increases from 14 for a humidity of 35 percent, to 22 for a humidity of 50, and drops back to 12 for a humidity of 100 percent. At 200 days, the corresponding figures are 14, 15, and 10. The matured cements thus have a lower coefficient of expansion than cements cured in humidities between 50 and 75 percent which at every age present a maximum that appears, moreover, to diminish with time. In any case, if the coefficient of expansion diminishes with age, it is always lower for curing in water than in air.

The coefficient of expansion is not independent of temperature, the average coefficient measured between 60° and 20° (return) is always less than that which is measured between 45° and 60° (outward); the dilation-temperature curves for outgoing and for return cannot be superposed except for a cement cured in water for a very long time. This phenomenon is probably due to the factor of physico-chemical transformations stimulated by the increase in temperature. For a normal portland cement, the extremes are a coefficient of 26×10^{-6} at the age of 20 days (between 45 and 60 °C) for a previous curing at 50 percent humidity and a coefficient of 10×10^{-6} at the age of 200 days and beyond for a previous curing in water. For a portland cement having a high initial strength, the maximum coefficient of 39×10^{-6} occurs between 45 and 60 °C at about 40 days for curing at 50 percent humidity; for a slag cement it is 25×10^{-6} at approximately the same age under the same conditions. The coefficient of expansion after long maturing in water is in both cases between 10 and 13×10^{-6}.

It is interesting to note that the average coefficient of expansion on the return between 60 and 20 °C of a paste aged 200 days varies with the quantity of water included, which depends on the previous state of curing. Figure 2 relative to a portland cement shows an increase with the water content followed by a decrease. This phenomenon has been observed by various authors, including D Bonnel and F. C. Harper [18] who in addition note that the desiccation of a concrete previously cured in water increases its coefficient of expansion and that the modulus of dilation of a saturated concrete is independent of its previous states of curing. It is therefore clear that the phenomenon is reversible and does not depend on the solid structure but solely on the presence of water. There is probably an interference between dilation and the phenomena giving rise to the hygrometric movement. It can be imagined that the diminution of the surface tension of the water with the temperature diminishes the shrinkage pressure [19] or that the increase of the vapor pressure of the water in the voids with the temperature produces a swelling pressure. These phenomena cannot occur in a saturated medium nor in the absence of free water. There must therefore be a maximum of swelling for an intermediate value (70 percent according to S. L. Meyers [20]). But this hygrometric swelling does not constitute a state of equilibrium and must disappear through the balancing of the water with its vapor at the same temperature. If we assume a swelling pressure given by Kelvin's expression $f=A\log\theta$, where θ is the relative humidity, the variation in pressure corresponding to a variation in temperature dt is:

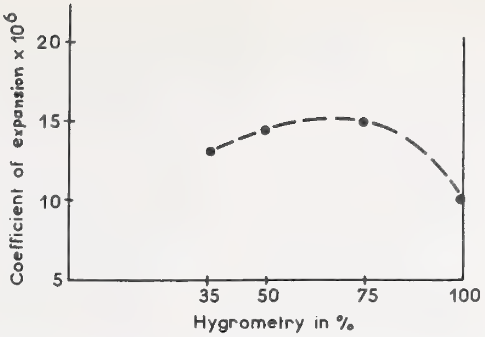

FIGURE 2. *Coefficient of expansion of a portland cement paste in relation to water content.*

$$\frac{df}{dt}=\frac{A}{\theta}\frac{d\theta}{dt}.$$

Now $\frac{d\theta}{dt}$ is nil for $\theta=1$ and nil for $\theta=\theta_i$, a humidity of equilibrium below which there is no longer any free water. We can write an approximate but simple function:

$$\frac{d\theta}{dt}\approx Q(1-\theta)(\theta-\theta_i).$$

Moreover, the swelling Δ must be proportional to the product of the swelling pressure by the quantity of water under pressure, $\frac{d\Delta}{dt}=s\theta E_0\frac{df}{dt}$ where E_0 is the water contained for $\theta=1$. Finally the expression of the instantaneous thermohygrometric swelling coefficient has the form:

$$\frac{d\Delta}{dt}=Q(1-\theta)(\theta-\theta_i)$$

which passes through a maximum for $\theta=\frac{1+\theta_i}{2}$.

If θ_i, the limit humidity of the free water, is 0.40, we find the maximum for $\theta=0.70$, which corresponds approximately to the tests and shows in any case that the reasoning is plausible.

Powers [21] finds an equally plausible explanation in saying that there is a capillary water and a water fixed in the gel that is constituted by the hydrated phase, the entropy of the capillary water and that of the gel being different. When the equilibrium is established, a change in temperature destroys this equilibrium and requires a transfer of water between the two phases. The delay in this transfer between the gel and the capillary water determines an additional dilation that disappears after reestablishment of the equilibrium. The same author indicates that cements autoclaved under steam pressure have a coefficient of expansion independent of the degree of humidity, which would be due to the replacement of the gel by a crystalline phase.

The coefficient of expansion of concrete depends on that of the aggregates. The variations in terms of age and of the curing medium are reduced in comparison with those that are found for the neat cement paste. The experiments that we have made show that the coefficient of expansion obeys the law of mixtures, taking account of the moduli of elasticity E_c of the pure paste cement and of the aggregate E_a:

$$\alpha_b=\frac{\alpha_a V_a E_a+\alpha_c V_c E_c}{V_a E_a+V_c E_c}$$

where α_a is the coefficient of expansion of the aggregate, α_c that of the pure paste, V_a the volume of aggregates and V_c that of cement.

For a concrete with limestone aggregate at 400 days of curing in air, the coefficient of expansion was 6.9×10^{-6}, that of the aggregate 5.5×10^{-6}, and that of the cement 14×10^{-6}. A similar concrete having quartz aggregate with a coefficient of expansion of 11.3×10^{-6} gave for the concrete 11×10^{-6}. A third concrete with mixed siliceous and Seine limestone aggregates had an expansion coefficient of 8.8×10^{-6}. The considerable importance of the role played by the aggregate in thermal expansion is apparent. This role has been recognized and studied by various authors, including D. Bonnel and F. C. Harper [18] and L. Mitchell [22] who have achieved results similar to ours—concretes with siliceous gravel, 13.2; granite, 8.6; sandstone, 11.7; crushed slag, 10.6×10^{-6}. It also appears that the coefficient of expansion diminishes with the cement content in a manner that also corresponds to the law of mixtures, taking account of the unpredictable deviations that this approximation entails.

It should be noted that the indications provided here concern only relatively low temperatures; beyond 200 to 250 °C we get a contraction due to dehydration followed by a fresh swelling from 400 °C on [23].

Shrinkage and Desiccation

A cement paste, or a concrete cured in humid air or in water, then placed in a dry atmosphere, will shrink and at the same time lose weight through evaporation of water. Replaced in water, they swell and regain weight through imbibition. There is thus a relation between the movement of the water and shrinkage that does indeed appear to be a cause-and-effect relationship. Various investigators have concerned themselves with this relationship [1, 24, 25, 26, 27, 28, 29, 30].

For a compact neat cement paste the relation appears to be linear (fig. 3) for an advanced age (OA). For a young paste, it is curvilinear (OB), the curve OB tending toward OA when the age of beginning desiccation increases. For a mortar and a concrete, the relation takes the form OCD. Up to a certain loss of water, of which the abscissa corresponds to OC, there is only a slight shrinkage; beyond this the deformation is proportional to the loss of water for an old cement and follows a certain curve for a concrete that has not completed its hardening.

But we are now concerned with an initial shrinkage of a cement paste or a concrete that has had no previous desiccation. Repeated cycles of desiccation-humidification show a residual shrinkage *Os* (fig. 4) taking account of a hysteresis of which the effect may increase or decrease according

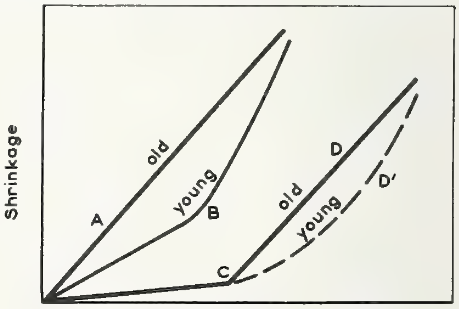

FIGURE 3. *Relation between loss of water and shrinkage of a cement paste.*

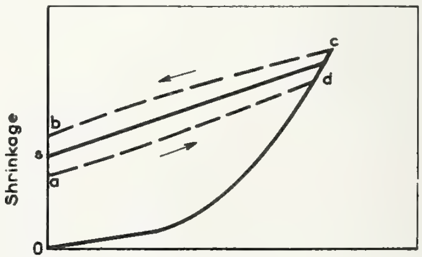

FIGURE 4. *Residual shrinkage after desiccation-humidification cycles.*

to the nature of the concrete and the degree of humidification. It can probably be explained as an effect of adjustment compensated by an effect of fatigue, both having a mechanical origin [28].

Beyond a certain degree of desiccation that practically can be obtained only by treatment at a temperature above 200 °C, it seems that a new relation can be attained in which shrinkage increases more rapidly in relation to loss of water.

All this seems to mean that, leaving aside possible transitions, what we have is different forms of water in regard to the shrinkage evaporation relation:

(a) a free water having little or no influence on the dimensional variations;

(b) a physically held water that is primarily involved in these variations;

(c) a water held at a higher degree that can be evaporated only under exceptional conditions of time or of temperature.

In the diagram of figure 5, the loss of water in terms of the degree of humidity of the curing medium can be expressed schematically by three straight lines: AB, free water whose quantity depends on the volume of the large voids in the paste; BC, water linked to shrinkage; CD, non-evaporable water [31].

It is interesting to know that a sample of cement protected against any evaporation by an impermeable coating during curing nevertheless shows shrinkage after a slight initial swelling [1]. This phenomenon shows that hydration has the effect of diminishing the internal humidity and leads to the same consequences as a progressive desiccation. This "adiabatic" desiccation, however, should not modify the hardening when the quantity of mixing water is such that $\frac{w}{c}>0.5$ [32]. It thus seems that the potential energy of hydration is higher than that which corresponds to evaporation above a certain hygrometric degree. The limit appears to be around 40 percent relative humidity for portland cement. The effect of diminution of humidity by hydration can occur only when the quantity of water chemically absorbed becomes greater than the quantity of free water. This effect is appreciable for pure pastes that contain little free water; after a year, the internal humidity can descend to 95 percent, a relatively slight drop [32]. (Lucas [33] indicates a limit of 85 percent for pure portland cement paste at 150 days.) For ordinary concrete such an effect is scarcely measurable.

Since shrinkage is for the major part conditioned by evaporation, it is interesting to know the laws that govern the latter. Figure 6 shows curves of variation in weight of concrete cured in different humidities, θ [31]. It might seem that we here have a phenomenon of capillary evaporation in which the latter would be zero at 100 percent humidity and total at 0 percent. Experience shows that the phenomenon is much more complicated. Atmosphere in which $\theta=0.99$ (we shall assume $\theta=0.99$, an arbitrary figure, and not $\theta=1$, for complete saturation leads to condensations impossible to control experimentally; here we have a discontinuity) may determine an evaporation or an increase in weight but never leaves the weight constant. Let us assume a spongy medium with large pores and such that the solid part has only a negligible affinity for water. Let us saturate it with water and place it in air. All the water will eventually evaporate, whatever may be the humidity, on condition that it is less than saturation. The water cannot subsist in the liquid state in the presence of an indefinite volume of air. There is in concrete a certain quantity of water that can be evaporated under these conditions. This quantity, in figure 6, is comprised between curve A of curing in water and the curve $\theta=99\%\simeq 100\%$, and is the value AB of figure 5.

It is difficult to define the law of this evaporation in terms of time. It begins with the wet surface where the speed of evaporation is constant,

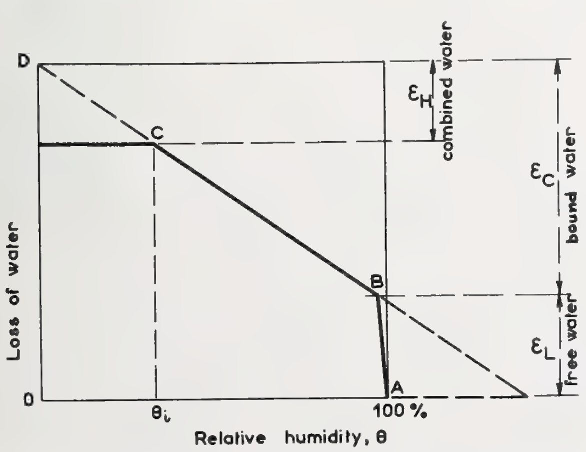

FIGURE 5. *Loss of water as a function of relative humidity.*

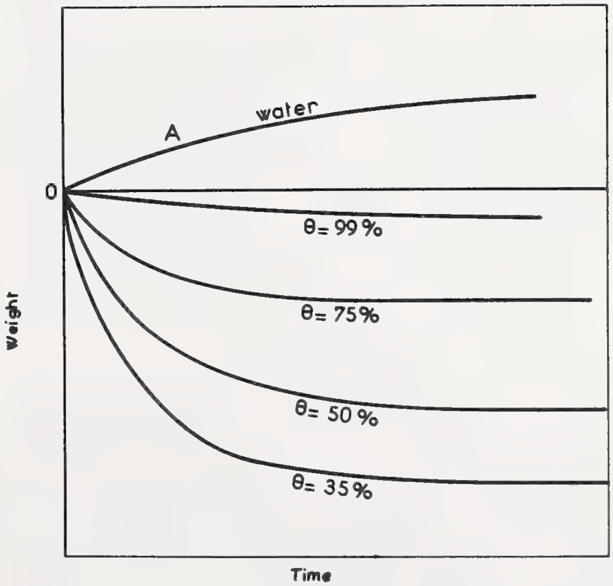

FIGURE 6. *Weight change of concrete cured at different relative humidities.*

then it diminishes until the concentration at the surface reaches a value in equilibrium with air. Finally, in a third period, a movement of diffusion of the internal water toward the surface begins. It is in fact this third phase that becomes all-important for the solid pieces in which the water from surface wetting is in small quantity compared with the free water of the pores.

In a one-dimensional medium, the movement of water at every point is defined by an equation $\frac{dE}{dt}=q(E)\frac{d^2E}{dx^2}$ where E is the quantity of water, x a normal geometric coordinate on the surface and $q(E)$ a function of E that remains to be specified and that represents a coefficient of diffusivity.

For a three-dimensional medium:

$$\frac{dE}{dt}=q(E)\left(\frac{d^2E}{dx^2}+\frac{d^2E}{dy^2}+\frac{d^2E}{dz^2}\right). \qquad (1)$$

It is a Fourier's equation with variable coefficients. It is difficult to find a solution to this equation. By operating empirically, one observes that the mean evaporation of a piece corresponds to an expression of the form:

$$\frac{dE}{dt}=-(E_L-E)\gamma(t) \qquad (2)$$

where γ is a function of time t elapsed since the beginning of the operation and E is the evaporated water.

If D is the designation given to the average dimension $D=\frac{\text{volume}}{\text{surface}}$, and K a coefficient of diffusivity peculiar to the solid, we observe that $\gamma(t)$ can be replaced by a function $\lambda\left(\frac{K}{D}, t\right)$ that is to say that the time necessary to obtain a determined evaporation is proportional to a certain function of the average dimension. We may write λ more simply in the form $\lambda\left[\frac{K^u}{D^u}t\right]$ where u is between 1 and 2.

By making $\tau=\left(\frac{K}{D}\right)^u t$, the preceding expression becomes:

$$\frac{dE}{d\tau}=(E_L-E)\left(\frac{K}{D}\right)^u\lambda(\tau) \qquad (3)$$

and the evaporated water:

$$E=E_L[1-e^{-\mu(\tau)}]$$

with $\lambda(\tau)=\frac{d\mu(\tau)}{d\tau}$.

This expression shows that the speed of evaporation is proportional to the quantity of remaining free water and appears to indicate that the movement of the water outward occurs within the liquid phase and not the vapor phase, at least for the most part. Equation (1) should then be written:

$$\frac{dE}{dt}=Q(E_L-E)\Delta^2_{xyz}E$$

and would have as a consequence that a perfectly dry barrier would oppose a transfer of humidity. Indeed the quantity of water that passes through a surface is $\left(\frac{dE}{dt}\right)_n=QE\frac{dE}{dn}$ where n is the direction of the normal. An experimental verification of this has been made on very fine sands [34], which appears to show that the transfer as the vapor phase is much slower than the transfer as the liquid phase, so that in order to take both into account we might write eq (1) in the form, from the saturated state:

$$\frac{dE}{dt}=[Q(E_L-E)+Q'E]\Delta^2E$$

with $Q'<<Q$.

Let us go back to eq (2) which indicates the speed of evaporation. Experience shows that the latter increases when the vapor stress diminishes, hence the function γ must include a term in θ, the relative humidity of the surrounding medium. For $\theta=0.99\simeq1$ the speed of evaporation is not zero.

In a first approximation, it seems that eq (3) can be written in the more precise form:

$$\frac{dE}{d\tau}=(E_L-E)\left(\frac{q}{D}\right)^u(A-B\theta)\lambda(\tau) \qquad (4)$$

in which now

$$\tau=\left(\frac{q}{D}\right)^u(A-B\theta)t \text{ and } \lambda(\tau)=\frac{d\mu(\tau)}{d\tau}$$

or

$$E=E_L[1-e^{-\mu(\tau)}], \qquad (5)$$

an expression still valid in a more general way if we write $\tau=\left(\frac{q}{D}\right)^u\varphi(\theta)$; $\varphi(\theta)$ being a decreasing monotonic function when θ increases, having a positive value for $\theta=0$ and a value, not zero, less than the preceding for $\theta=1$.

All this is very theoretical and in fact presents only a phenomenological aspect, but one that it is interesting to consider for it will guide us in the realm of bound water. If we call the bound water E_c, whether it be capillary, adsorbed, or colloidal, it slowly gets into equilibrium with the relative humidity θ. Between certain limits, $\theta=0.99$ and $\theta=0.4$ for example, $E_c=\theta E_C$ when equilibrium is reached (fig. 5). However the evaporation of the bound water and that of the free water are not totally separate; they partly overlap, for concrete is a heterogeneous medium both in its structure and in the mechanism of evaporation which is itself heterogeneous in the volume once the surface has reached a sufficient dryness: $\theta<0.99$.

By analogy with the evaporation of free water but knowing that the evaporable part of the bound water diminishes when the humidity increases, we can write:

$$E=E_c(1-\theta)[1-e^{-\eta(\tau)}] \tag{6}$$

where E_c represents the bound water and $\tau=\left(\frac{K}{D}\right)^u t$ so that the speed of evaporation is:

$$\frac{dE}{dt}=[E_c(1-\theta)-E]\left(\frac{K}{D}\right)^u \nu(\tau);$$

$$\nu(\tau)=\frac{d\eta(\tau)}{d\tau}. \tag{7}$$

The only distinction that can be made in relation to eq (4) is that $\frac{dE}{dt}$ is annulled for $\theta=1$ and $E=0$.

Even more generally, we could write:

$$E=E_c\Phi(\theta)[1-e^{-\eta(\tau)}]$$

but it is possible, in a first approximation, to let Φ keep a linear form.

The function $\eta(\tau)$ remains to be defined. It is easy to represent it in an empirical manner as a power of τ, or $\eta(\tau)=\left(\frac{K^u}{D^u}t\right)^{1/n}$. But K itself is a function of age a since the concrete hardens and becomes less permeable; we shall write:

$$K=\mathrm{K}\left[\frac{\alpha}{(a+t)^{1/m}}+\beta\right].$$

Experiments show [31, 34] that n is close to 2; as for the variation of K, it is different depending on the composition. For a pure paste, we find that β is small compared with $\frac{\alpha}{(a+t)^{1/m}}$, with m close to 3, whereas for a concrete the variation of K is slight, m is above 12.

Finally, we shall write:

$$E=E_c(1-\theta)\left[1-e^{-\left[\frac{K(t)}{D}\right]^{u/2}\sqrt{t}}\right]$$

where $K(t)$ is a decreasing function during hardening, tending toward a constant value with age.

The quantity of bound water evaporated, E_c, at a given moment, may be determined by placing the test piece in a saturated atmosphere and maintaining it long enough (fig. 7). The gain of weight corresponds to E_c. A similar test piece placed in water takes on greater weight and joins the curve that corresponds to the permanent maintenance in water. The difference corresponds to the evaporated free water E_l.

We must now go on to the relation $\Delta(E_c)$. If we represent in juxtaposition figure 6, which gives the water variation, and figure 8, which indicates the volume or average length variation, and we look for a correlation between these two magnitudes for each value of t, we find that the correlation is approximately linear. We do not want to say here that a better approximation is impossible, but in the present state of knowledge it is difficult to do better.

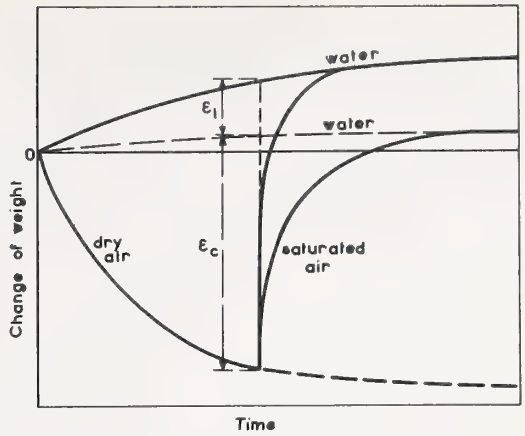

FIGURE 7. *Determination of bound and free water evaporated.*

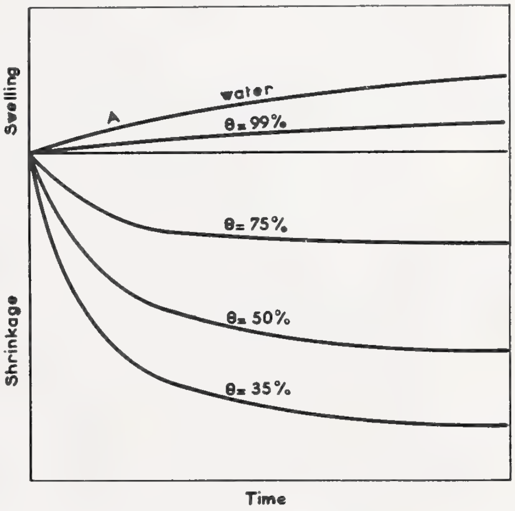

FIGURE 8. *Volume change of concrete cured at different relative humidities.*

We shall thus write:

$$\Delta=\rho(E_l-E_L) \qquad E_l>E_L$$

where E_l is the evaporated water, E_L the total free water, and ρ a coefficient of shrinkage. This relationship leaves out of account other influences such as the action of carbon dioxide and that of the internal stresses produced by shrinkage. Experiment shows that the coefficient of shrinkage varies with age a and increases with time t. An identical loss of water gives a greater shrinkage at 1,000 days than at 7 days. This result, surprising at first sight, can be explained if we recall that the quantity of hydrated cement also increases with time and we can admit the hypothesis that ρ is proportional to the volume of the hydrated phase or, if one prefers to reason from the gel, to the volume of gel formed. We shall say more simply by taking water as a variable that ρ is proportional to E_h, the quantity of water absorbed by hydration.

Finally, it must be possible to express the law of shrinkage in the form:

$$\Delta(t)=QE_h(E_\iota-E_L) \tag{8}$$

$$\Delta(t)=QE_h(t)E_c(1-\theta)[1-e^{-\eta(\tau)}] \tag{9}$$

with $\tau=\left(\frac{K}{D}\right)^u t.$

We may note that this gives for the differential element:

$$\frac{d\Delta}{dt}=QE_h\frac{dE}{dt}+QE\frac{dE_h}{dt}.$$

If we consider the proportionality to the differential element only, this leads us to write:

$$\frac{d\Delta}{dt}=QE_h\frac{dE}{dt} \tag{10}$$

and the speed of shrinkage is less.

This proposition appears more correct but leads to an equation difficult to integrate in an analytical manner, especially as $E_h(t)$ is inexactly known. In any case, the final shrinkage remains the same and proportional to $(1-\theta)\frac{K}{D}$. In order to avoid having to make calculations on hypothetical bases, it appears possible and especially prudent to write simply:

$$\frac{d\Delta}{dt}=[\Delta_m(\theta)-\Delta]\left(\frac{K}{D}\right)^u\chi(\tau)$$

where χ is a function to be determined experimentally, and if we admit the linearity of the final shrinkage in terms of θ: $\Delta_m(\theta)=\Delta_M(1-\theta)$ where Δ_M is a reference value for $\theta=0$. We shall see later that it cannot be affirmed that this last relation is correct.

Finally:

$$\Delta(t)=\Delta_m(\theta)[1-e^{-\Phi(\tau)}] \tag{11}$$

where $\chi(\tau)=\frac{d\Phi(\tau)}{d\tau}$.

In the case of application of eq (8): $\chi(\tau)=\nu(\tau)$ (see eq (7)), the form of the shrinkage curve would be the same as that of the curve of evaporation of the bound water. So it is for aged concretes, but young concretes diverge slightly (fig. 3), which appears to justify eq (10).

A consequence of the theory that has just been put forward is that the final shrinkage in atmosphere θ must be independent of the previous curing up to an age a (this is confirmed by Dutron [11]). Only the speed of shrinkage from the age beyond which θ is constant is modified. Figure 9 which results from our tests shows the shape of the shrinkage curves. We see that the low shrinkage rate at advanced ages can partially mask the phenomenon. It is, moreover, possible that in solid pieces the development of internal stresses may lead to irreversible plastic deformations whose resultant opposes contraction. It may be supposed that the final shrinkage somewhat diminishes with the age of loading, all the more so as the mean dimension D is greater. It will be further remarked that if the measured swelling in water is important the shrinkage can diminish after a certain time. We have observed this phenomenon after several years of curing [7], indicating, therefore, that the physico-chemical swelling referred to above persists even in dry air.

We have already given a function of shrinkage depending on the time in which we find in the e power another function $\Phi(t)$ which governs the whole phenomenon. This function must depend on the age a of placing in dry air and on the time t, in other words on the two variables t and $(t+a)$.

It seems that they can be given the same form as that which we had recourse to for the evaporation, so that, finally:

$$\Delta=\Delta_m(\theta)\left[1-e^{-\frac{K(t)}{D}\sqrt{t}}\right]$$

An important phenomenon to consider is the reversibility of shrinkage. By contrast with what we observe for the variation in weight, the reversibility is not complete even after a prolonged immersion in water. A permanent deformation δ subsists, such that $\frac{\delta}{\Delta}$ varies between 0.3 and 0.6. We are entitled to wonder to what this is due. It immediately suggests a plastic phenomenon, but it is not certain that this similarity is in fact representative. If such were the case the deformations would be due to a shrinkage pressure

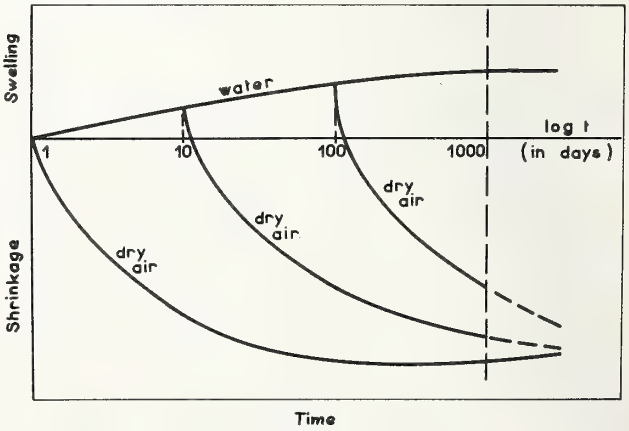

Figure 9. *Drying shrinkage in relation to previous curing.*

resulting from inner stresses but which would modify the rupture conditions. Now, these do not appear to be affected by the shrinkage in an appreciable manner before the stresses that would enter into play. An explanation must therefore probably be sought elsewhere. The question has not yet been answered, but it seems that it may be at least partially answered by the introduction during shrinkage of additional links due to the progress of hydration in the condensed medium, that is to say to the creation of new links through the coming together of the crystallites that oppose swelling, at the moment of the return to the wet medium. In favor of this explanation we observe that the residual shrinkage disappears when concretes have undergone a prolonged hardening in water (180 days for example) before placing in dry air [1]. In addition to which we shall see later that carbonation, which generates a structure insensitive to moisture, increases the residual shrinkage considerably.

This theoretical part which we conclude herewith and which rests on our personal investigations [35] must be compared with the studies of other authors. Those of Lucas [33] appear to indicate that between relative humidities of 40 and 99 percent, evaporation and shrinkage are approximately linear functions of θ; below 40 percent, the curves assume a somewhat irregular appearance. It is observed, moreover, that swelling in water becomes more pronounced after desiccation at less than 40 percent, which seems indeed to show a cessation of hydration in these very low humidities. Haller [36] clearly brings out the linear relation between the evaporated water and the humidity, but this relation does not appear precisely for the shrinkage, whereas it is more or less observed in Dutron's tests [11].

Finally it may be said that the assumption of linearity between certain limits of humidity $\theta=0.4$ and $\theta=0.95$ appears to be approximately acceptable for evaporation.

On the other hand, it is not certain that this is always the case for shrinkage. The curves obtained in terms of θ are in general of the form given by figure 10 in relation to the saturated state in water. AD represents the swelling in water in relation to curing at 99 percent rh. But nothing tells us that for $\theta<99$ percent there is not a swelling being deducted from the shrinkage, such swelling being always possible in the presence of free water so long as any subsists in a part of the volume. The theoretical shrinkage curve BC is thus modified by the swelling s which is greater as the value of θ is higher.

This point of view appears to be confirmed by the fact that concretes cured for a very long time (more than a year) in water show a shrinkage, when placed in air, that is really proportional to $(1-\theta)$; the swelling then becomes negligible in relation to the shrinkage that subsequently occurs.

Finally it is necessary to explain why certain cements such as slag give in neat paste and in rich mortar a marked shrinkage at 99 percent of relative humidity. We believe that this shrinkage is due to the inner desiccation caused by hydration which produces a shrinkage without variation in weight of the parts furthest removed from the surface. The straight line i of figure 10 which represents the initial length passes below D.

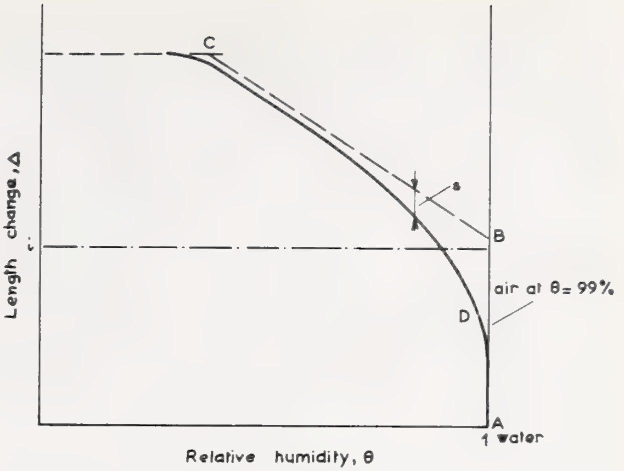

FIGURE 10. *Combination of swelling and shrinkage.*

A natural factor that plays an important role in shrinkage is atmospheric carbon dioxide. It has been studied in particular by Meyers [37], Leber and Blakey [38], and Verbeck [39]. Prisms of mortar placed in an atmosphere of carbon dioxide at the same relative humidity show an increase of shrinkage and an increase in weight. This increase is zero for saturated atmosphere, approximately double the normal shrinkage for $\theta=50$ percent where it reaches a maximum, and tends toward 0 for $\theta<25$ percent. We see that this influence is far from negligible and must be appreciable even for atmospheric air. It seems, moreover, that this effect increases with the dimension of the sample and thereupon decreases. It is therefore not surprising that such a phenomenon should modify the aspect of the theoretical curve of shrinkage and give it different shapes according to the experimental method used.

It appears moreover that carbonation diminishes the reversible part of the shrinkage and subsequently gives it a greater stability during the alternations of drying and moistening. This is the proof of the presence of a supplementary solid structure that does not have the hydroconstrictive properties of the hydrated phase of the cement. We therefore recommend to experimenters that they carry out shrinkage measurements in atmospheres free of carbon dioxide which may distort the results in a manner that is unexpected and difficult to control; this is now the procedure in our laboratory.

The volumetric coefficient has been studied by Ross [40], Haller [36], Glanville [41], and Carlson [42]. It is found that the shrinkage in dry air of prisms of pure paste having section ratios of

1 to 2 is in the ratio of 1.3 to 2.3 at 1 yr and tends toward 2.5 for section ratios of 1 to 8. Ross's tests show how the shrinkage propagates from a free surface in a plate made impermeable at all the other surfaces. At 200 days, the shrinkage at a distance of 4 in from the surface is still only one-third of the surface shrinkage. This delay is considerable, and its order of magnitude can be roughly fixed as proportional to the square of the distance to the surface of evaporation. If we compare the shrinkages as well as the losses in water of different test pieces of the same concrete tested by Ross [35], we find that the values align themselves along a single curve in relation to the variable $t\left(\frac{s}{v}\right)^2$. This means that the time necessary to produce a given shrinkage is proportional to the ratio $\left(\frac{v}{s}\right)^2$, other things being equal as far as the composition and the curing medium are concerned. Karapetian [79] indicates that for a block dried at 50 percent rh desiccation reaches 8 cm in depth at the end of a month and 60 cm at the end of 10 yr (the term "dried" probably means that the concrete has lost its free water).

Our tests confirm this point of view insofar as atmospheres of high humidity are concerned. On the other hand, for shrinkages carried out at a low humidity, lower than 50 percent rh, the exponent u of formula (3) and the following appears to tend toward unity [80]. This is why we wrote above that the exponent u was between 1 and 2.

We may note that Weil [81] gives shrinkage values in terms of the dimension which bring out exponent u close to 1.5 while Karapetian's results [79] give a value close to 2. Practically, apart from exceptional desiccations, it seems that we may take $u=2$ as a first approximation.

Composition

The part played by the composition of the concrete is very important in creating shrinkage. First of all the nature of the cement has a considerable influence. Roughly speaking, shrinkages increase in the following order: ordinary portland, aluminous cement, slag, and portland with high early strength. In each category, they are very variable. According to Cocagne [35] an ordinary portland gives 0.22 percent shrinkage in neat paste at 1,000 days, a portland having high early strength 0.35 percent. Dutron [11] indicates for ordinary portland a figure of the same order of magnitude, for aluminous cement, 0.25 percent. The same author shows that in portland and slag mixtures, the shrinkage increases with the proportion of the latter. Figure 11 gives a number of average curves relating to cements manufactured in France.

Graf [43] seems to have been the first to concern himself with the influence of the grain size of the cement on shrinkage by bringing out the increase of the latter when the specific surface increases. Haller [36] has shown that shrinkage increases from 0.117 to 0.169 percent in 90 days when the specific surface increases from 1,355 cm^2/g to 2,280 cm^2/g for the same portland cement. Jaspers [44] finds a linear relation between the specific surface and shrinkage at 90 days. Lafuma [45] likewise

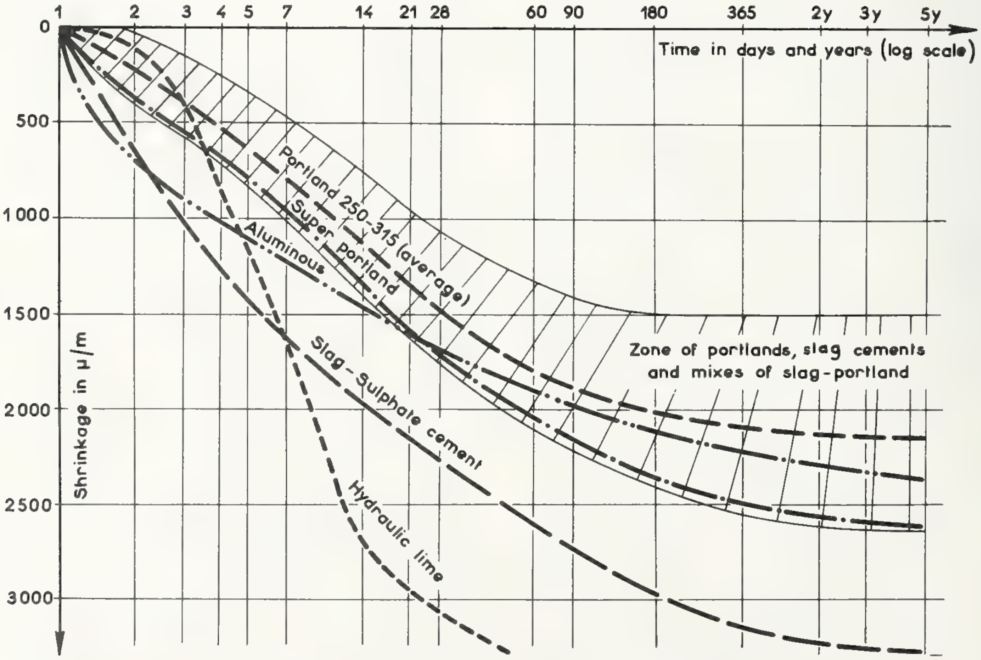

FIGURE 11. *Shrinkage of some cements in pure paste.*

According to Centre d'Etudes des Liants Hydrauliques, Paris. Tests on samples 4 x 4 x 16 cm at 50 percent rh and temperature 20 °C.

brings out a variation of the same kind on mortar: from 2,000 to 5,500 cm^2/g obtained with the same clinker the shrinkage increases from 0.05 to 0.17 percent while the losses in weight are less for the highest specific surfaces. The latter fact confirms what we had already established, that with an identical quantity of evaporated water, shrinkage increases with the volume of the hydrated phase, and this volume does increase with the specific surface.

The addition of mineral powders to the cement may have variable effects; certain authors [11] indicate a marked increase. Our tests carried out with mixtures of cement and basalt powder [1] have indicated, on the contrary, an increase in shrinkage with the cement/powder ratio. There is accordingly an influence exerted by the mineralogical nature of the filler.

The introduction of soluble salts into the mixing water, apart from a chemical reaction of expansion, has the effect of increasing the shrinkage [46]. The salts dissolved in the city water contribute an appreciable increase. Sodium carbonate at 0.4 percent in the mixing water increases the shrinkage at 1 month by 40 percent, sodium nitrate at 6 percent doubles the shrinkage. But the most specially studied influence was that of calcium chloride habitually used as an antifreeze and hardening accelerator [47]. The experiments that we have made [7] have shown a marked increase in the shrinkage of an ordinary portland measured at 5 months from the introduction of a quantity of $CaCl_2$ equal to 0.5 percent of the weight of cement. This increase of approximately 50 percent persists without great variation to 2 percent of $CaCl_2$, then from this quantity the shrinkage suddenly increases, its increase amounting to 110 percent for 2.5 percent of added $CaCl_2$ and 165 percent for an addition of 3 percent of $CaCl_2$.

Let us now examine the influence of the quantity of mixing water in mortars and concretes. Certain authors, including Haller [36] and Cocagne [48], indicate a rather important increase in shrinkage with the ratio $\frac{\text{water}}{\text{cement}}\left(=\frac{w}{c}\right)$. But this increase occurs with neat pastes. In the case of a concrete, our tests have shown a very slight influence both on shrinkage and on swelling when it is considered after a day of hardening, the first shrinkage being on the contrary influenced by variation of this ratio as was said at the beginning of this paper and as Pickett [49] confirms. For a portland concrete with a cement content of 350 kg/m^3 and Seine aggregates, the shrinkage at 1,000 days was 0.045 percent for $\frac{w}{c}=0.47$, 0.048 for $\frac{w}{c}=0.52$, and 0.05 percent for $\frac{w}{c}=0.57$. Which is to say that the variations are of the order of magnitude of the experimental errors while the limits of $\frac{w}{c}$ correspond to the extreme possibilities of placing. Another series of tests covering several thousand concretes studied from the statistical point of view have shown that the variation of $\frac{w}{c}$ possible for the range of cement contents extending from 250 to 500 kg/m^3 had an influence on shrinkage amounting to less than 10 percent [50].

As the losses in weight, moreover, are approximately proportional to $\frac{w}{c}$ this result seems to mean that beyond a certain quantity of mixing water, the incorporated water becomes free water without appreciable influence on shrinkage. The same is obviously not true for neat paste, where the $\frac{w}{c}$ ratio is less at normal consistencies.

The cement content, on the other hand, has a very marked influence. Many authors have studied it [48, 11, 36, etc.].

It seems that a usable empirical expression is here possible. Dutron indicates for the shrinkage of concrete:

$$\Delta_b=\gamma(e+c+v+f)^n$$

where e=volume of water, c=volume of cement, v=volume of voids, f=volume of fines. If the volume of the aggregate is written $a=[1-(e+c+v+f)]$ and if $a=0$ we obtain the shrinkage of the neat paste Δ_c and this expression becomes transformed into $\Delta_b=\Delta_c(1-a)^n$. We find that n is between 1.20 and 1.70 when the tests of the different authors are interpreted. (Pickett [49], who has established this formula theoretically, finds $n=1.7$.) Our measurements on siliceous Seine aggregates (silex) gave $n=1.24$ with a maximum spread of 10 percent.

Another semiempiric expression proposed by us [31] has the form:

$$\Delta_b=\Delta_c\frac{c}{c+[1-(c+e+v+f)]\mu_{ca}}=\Delta_c\frac{c}{c+a\mu_{ca}}$$

where μ_{ca} is a coefficient that represents the relation between the coefficient of compressibility of the aggregates and that of the cement paste. For a siliceous aggregate we find that $\mu_{ca}=0.88-0.53\ \frac{w}{c}$. The mineralogical nature of the aggregate has a marked effect on the amount of the shrinkage as may be expected from the above formula. Numerous investigators among those already quoted have taken this factor into consideration. Figure 12 shows the results of tests on a concrete with a cement content of 350 kg/m^3 with an identical quantity of water $\left(\frac{w}{c}=0.55\right)$ and aggregates of different mineralogical natures. This variation is quite adequately expressed in the preceding formula by the variation in the modulus of compressibility.

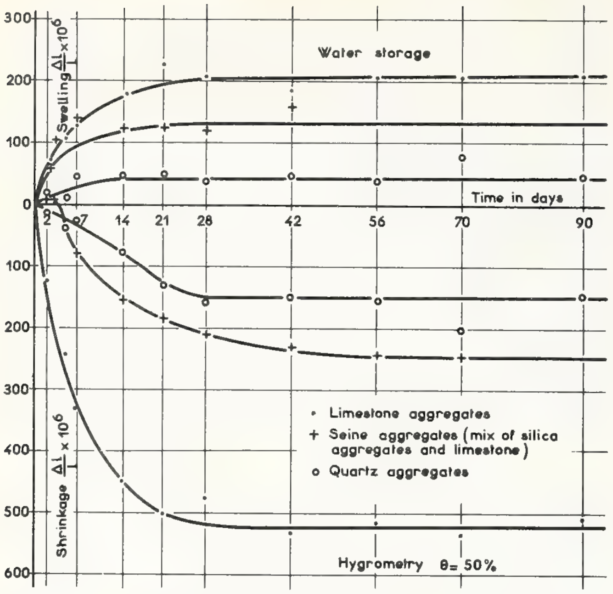

FIGURE 12. *Swelling and shrinkage of concrete with different aggregates.*

Theories

How is shrinkage to be explained? The answer to this question appears not an easy one.

One of the first theories is that of shrinkage stress (or of swelling stress) in which the liquid phase is placed under stress in relation to its initial state. Let F be this stress, e the liquid volume, v the total volume of the solid phase. The shrinkage should be:

$$\Delta = F \frac{e}{v} \chi_b$$

where χ is a coefficient of compressibility of the solid.

In order to determine F it is assumed that the stresses that can be developed are capillary stresses. This idea appears to have been put forward initially by Freyssinet [51]. It has since been adopted by various authors and almost completely abandoned [19]. The force F in this case should be proportional to the surface tension σ of the liquid that fills the capillaries and inversely proportional to the radii of curvature r_1 and r_2 of the menisci that limit the liquid phase, or

$$F = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right).$$

If the quantity of water diminishes, the radii do likewise and F increases.

Kelvin's equation, moreover, gives

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{AT}{\sigma} \log \theta$$

where T is the absolute temperature, and

$$F = AT \log \theta,$$

which makes it possible to set aside the artifice of capillarity, and finally the shrinkage would be:

$$\Delta = ATe \log \theta.$$

But such a relation can be considered valid only between certain limits, for if θ diminishes, e likewise diminishes, and Δ must pass through a maximum for the decreasing θ, which is contrary to experience. Calculation shows without difficulty that if we write $e = e_l + e_j(1 - \theta)$, $\frac{e_l}{e_j}$ must be greater than 0.40 in order that the shrinkage may be stabilized approximately within $\theta = 0.25$, and under these conditions the calculated shrinkage varies but slightly from linearity up to $\theta = 0.5$.

If e_l is a kind of nonevaporable water, hence of hydration water or water fixed in such a way that it cannot escape for very low humidities, it must itself be placed under the same stress as evaporable water. This hypothesis remains to be proved and has a somewhat artificial aspect. Nevertheless, such a mechanism is not in contradiction with the hypothesis that presents the hydrated phase in the form of a gel.

The other hypothesis that assumes that the water is deposited on the solid crystallites having great surface development in adsorbed layers is likewise plausible. The evaporation of the outer layers, the least bound, develops forces of attraction on the inner water layers, by liberation of the Van der Waals forces, which place the adjacent solid in compression, by reaction, the last layers being too tightly bound to the solid to be extracted. The mass of water thus conserved may be sufficiently small to be confused with the hydration water. We may then attempt to get an idea of the magnitude of these forces of attraction by suction measurements. We know that a porous body placed in the presence of free water absorbs this water by exerting a tension on it that depends on the quantity of water e already contained in this body [52]. This force F can be measured by preventing the penetration of the water by means of a reduced pressure exerted on the latter. We then find that F is a function of the water contained in the body at the moment when the measurement is made; $F(e)$. The suction is generally expressed as a decimal logarithm of the height of water in cm corresponding to the suction F: $pF = \log_{10} H$. Beyond $pF = 3$, that is to say beyond atmospheric pressure, the device using suction on the liquid phase is no longer usable. We then use a drier in which the sample is suspended in the void above a solution of sulfuric acid of known density which, at equilibrium, gives a relative humidity θ. The value of the suction is then given by Kelvin's formula, and for a temperature of 20 °C

$$pF = 6.5 + \log_{10}(2 - \log_{10} \theta).$$

We then obtain for the cement a curve of the form given by figure 13. One can also attempt to extract the water and measure the necessary force by proceeding according to one of the two above methods and, further, by centrifuging. The $pF(e)$ relation found then gives a curve that is above the previous one (fig. 13). It is to be regretted that very few attempts have been made to connect suction with the variation in the volume of the cement.

What we observe, however, is that drying develops a higher pF than moistening, the quantity of water being equal, and this effect may be favorable to the creation of a residual shrinkage. It is nevertheless possible to examine whether the order of magnitude of the suction forces is sufficient to explain the shrinkage deformation. Let us assume that we have reached $pF=5$ for 50 percent of evaporated water; this gives $F=100$ kg/cm^2. Let us further assume that the water that remains at this humidity represents 50 percent of the volume of the cement. The hydrostatic pressure on the solid part is then at the maximum: $p=100\times 0.4=40$ kg/cm^2. The elastic deformation that corresponds to the saturation of the paste is of the order of

$$\Delta=p\,\frac{1-2\sigma}{E}$$

With $E=200{,}000$ kg/cm^2 and $\sigma=0.2$, we should find

$$\frac{\Delta l}{l}=80\times 10^{-6}=0.008\%.$$

The order of magnitude of the deformations measured is more than 0.1 percent. The part of shrinkage deformation corresponding to the suction forces is of the order of one-tenth of the total deformation, and the suction forces cannot alone explain the shrinkage.

An interesting remark to be made derives from the observations of shrinkage on cements and concretes treated by heat. A treatment at 80 °C for 3 hr does not markedly modify the resulting shrinkage, whereas a treatment at 185° for 8 hr under a pressure of 10 atm of saturated steam completely changes the phenomenon. We first observe in neat paste a very considerable swelling during the treatment (between 0.1 and 0.6 percent) if the test piece remains free to dilate. But whether the freedom is allowed or the mortar is kept in a closed mold, we find that the shrinkage measured upon drying after cooling becomes very slight, between 1.0 and 2.0 percent of the shrinkage measured on an untreated control concrete [53]. This shrinkage is then of the order of magnitude of that indicated above under the influence of the suction forces alone. Now, we know that the silicate crystals hydrated at high temperature have a different structure and a greater volume stability. It is then possible that the origin of the shrinkage is to be found in large part in the crystalline structure and that in the case of treatment by autoclave the crystals formed are no longer sensitive to variations in humidity. It is well then to look for the origin of this sensitivity.

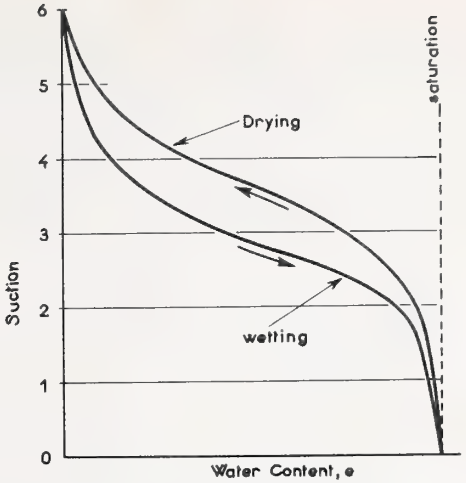

FIGURE 13. *Form of curves of wetting and drying of cement.*

In his work on the structure of hydrated cements, Bernal indicates [54] the presence of tobermorite in fibrous form and, in the direction normal to the fibers, of layers of water the thickness of which varies from 14 to 9 A during drying. This is no longer a simple phenomenon of adsorption but of layers of zeolitic water of dimensions varying with the humidity of the medium. It is Bernal's opinion that we must look here for the origin of the shrinkage properties of cement. In concretes hydrated under heat, tobermorite crystallizes mainly in the form of slabs and no longer in the form of fibers, such slabs being probably less sensitive to the hydroconstrictive movement. Powers [21] appears to be of a different opinion and finds an explanation by saying that for setting at normal temperature the hydrated phase appears in a colloidal form highly sensitive to humidity whereas the treatment by steam under pressure gives a crystallized and not a colloidal phase. He bases this explanation on the fact that cements treated in this manner have a coefficient of thermal expansion independent of humidity.

Volume Variations of Concrete Under Load

Under a progressive loading applied at a given age, concrete undergoes a deformation. Let us call this deformation Δ measured in a part uniformly stressed and T the corresponding homogeneous stress, whether of tension or compression. T is shown as the ordinates and Δ as the abscissas of a system of rectangular coordinates (fig. 14), and we get a curve of deformation. This curve OA is tangential to, or one with, a straight line OE over a certain length (an inflection at the

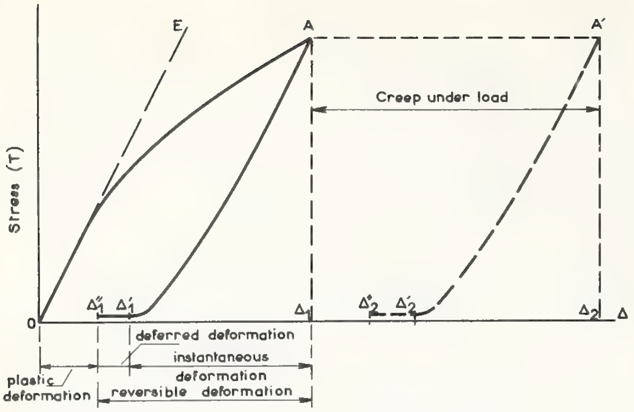

FIGURE 14. *Stress-deformation relations for concrete.*

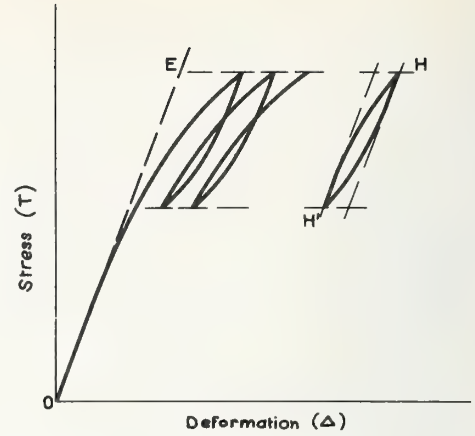

FIGURE 15. *Stress-deformation relation on cyclic loading.*

beginning of the compression curve can sometimes be observed; this is the sign of a preexisting internal microfissuration).

After having applied the load as far as A, let us remove the load. The unloading curve is close to a straight line but very slightly incurved in the opposite direction. After complete removal of the load, there remains a deformation Δ_1' and, after a time of rest, the residual deformation diminishes by a slight amount and tends toward Δ_1''. If the load removal is sufficiently rapid, the instantaneous reversible deformation is called $\Delta_1-\Delta_1'$, the reversible total deformation $\Delta_1-\Delta_1''$, and the reversible deferred deformation $\Delta_1'-\Delta_1''$, while the permanent residual deformation or plastic deformation is Δ_1''. If the solid is maintained under load a sufficiently long time, the deformation increases from A to A′ and reaches the value Δ_2. The magnitude $\Delta_2-\Delta_1$ is the creep under load, while $\Delta_2''-\Delta_2'$ is the residual creep. If instead of completely unloading the test piece the stress is partially decreased and load is again applied, and the process is repeated a certain number of times, one obtains a series of loops that finally stabilize in the form of a very flattened loop HH′ practically identical with a straight line (fig. 15). The inclination of this straight line is the same as that of the original tangent OE. This property is verified when the maximum load is less than 6/10 of the breaking load. The modulus of elasticity thus defined, or fundamental modulus, is the same as the one found by means of the measurement of the speed of propagation of shock waves [55]. Because of this it is called "modulus of dynamic elasticity".

As the total deformation of a concrete includes an elastic and reversible part and a plastic part, it is necessary in order to recognize the relative parts to operate through successive and increasing loadings with intervals of unloading. Three curves can thus be established (fig. 16): the curve of total deformation Δ_T, the curve of plastic or residual deformation Δ_R and the curve of elastic deformation $\Delta_E=\Delta_T-\Delta_R$.

Finally, if for a compressive or tensile stress the deformation δ is measured in the direction normal to that of the applied total stress, the latter has a sign which is the contrary of the longitudinal deformation Δ. We can recognize in δ a total deformation δ_T, a residual deformation δ_R and a reversible elastic deformation δ_E. From which we obtain three values to be considered:

—the total Poisson's ratio, $\sigma_T=-\dfrac{\delta_T}{\Delta_T}$

—the plastic Poisson's ratio, $\sigma_R=-\dfrac{\delta_R}{\Delta_R}$

—the elastic Poisson's ratio, $\sigma_E=-\dfrac{\delta_E}{\Delta_E}$.

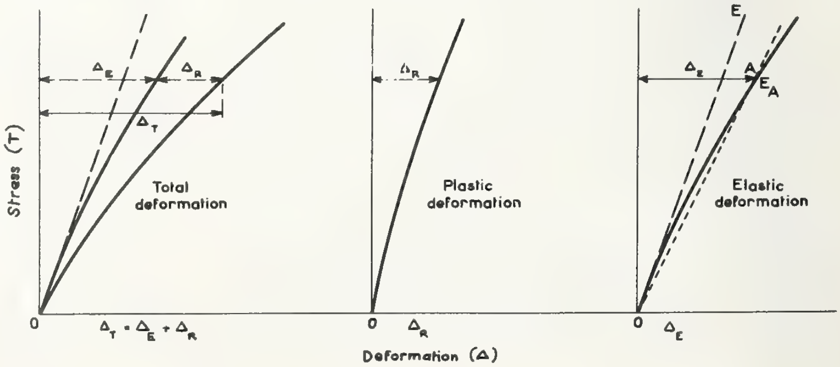

FIGURE 16. *Curves of total, plastic, and elastic deformation of concrete.*

These preliminaries having been effected in order to narrow the definitions, we shall successively examine the elastic deformation of concrete, its rapid plastic deformation, and its slow plastic deformation or creep in terms of the variables already considered for the study of shrinkage, to which is added the variable stress T.

Elastic Deformations

Experience shows that $\Delta_E(T)$ is not a straight line and that concrete has an elasticity that is not perfectly linear, but this lack of linearity is not very great and diminishes when the concrete ages. If we define the modulus of elastic deformation or secant modulus $E_A=\frac{T}{\Delta_E}$ (fig. 16) as the inclination of the straight line OA that joins the origin to point A considered on the curve, it is possible to examine its relative variation in terms of the stress T and its relation to the classical instantaneous breaking load R (on cylinder). The experimental work done on this subject is rather limited, for the authors have neglected, in most cases, to separate the reversible elastic deformation from the total deformation.

It is recognized that $\frac{E_A}{E}$ remains constant up to one-tenth of the rupture load. Le Camus [56] has found that $\frac{E_A}{A}=0.95$ for $\frac{T}{R}=0.2$, 0.90 for $\frac{T}{R}=0.33$, and 0.75 for $\frac{T}{R}=0.5$.

The Federal Laboratory of Zurich gives the formula:

$$\frac{E_A}{E}=\frac{1}{1+K\frac{T/R}{1-T/R}}$$

with $K=0.10$ (it seems that for young concretes, K should be higher, close to 0.25). Santarella [57] indicates that the modulus of elasticity diminishes in an almost linear manner till it reaches one-half the breaking load. Vivian [58] gives for the modulus E_A a formula that leads to $\frac{E_A}{E}=0.97$ for $\frac{T}{R}=0.10$, 0.94 for $\frac{T}{R}=0.20$, and 0.92 for $\frac{T}{R}=0.30$. We see that all these results do not greatly differ. When concrete is loaded at increasing speed, the modulus E_A measured at 50 percent of the breaking load increases to join the modulus of dynamic elasticity E [59]. This behavior appears to show the presence of a viscous elasticity, the ratio of viscosity depending on the load, the curve of elastic deformation approaching a straight line for increasing speeds of stress.

For a given concrete, the modulus of elasticity increases with age during hardening in accordance with a law that is approximately proportional to the square root of the compressive strength, and it is greatly influenced by the humidity of the curing medium. Our tests have shown, for example, on a concrete containing 350 kg of cement per m^3, with siliceous aggregates, the following moduli at 200 days:

Relative humidity of curing medium	Modulus of elasticity
%	*kg/cm²*
35	340, 000
50	365, 000
75	385, 000
99	450, 000
Water	450, 000

It is to be noted that a concrete cured in dry air and subsequently exposed to humidity does not recover the modulus of elasticity of the same concrete cured uninterruptedly in moist air; the modulus does increase, but remains definitely lower. It is therefore probable that the mode of hardening of a concrete cured in dry air does not lead to the same structure of the hydrated phase. The formation of gel or of crystals cannot occur in voids from which water is absent. A curing in water for a week followed by exposure to dry air does not appear, on the other hand, to modify substantially the subsequent increase in the modulus that proceeds as for a curing in water. It must be, then, that the curing during the early stage is predominant, permitting the creation from the beginning of a more compact structure that subsequently becomes consolidated.

The modulus of elasticity of concrete is influenced by the variations in composition, in compactness, and in physical or chemical decomposition. This sensitivity, bearing in mind the scatter, is at least as great as that observed in tests for mechanical strength. In addition, it confers upon the measurement the advantage of applying to a volumetric mean, and in the case of the use of dynamic methods (speed of sound) it brings out a localized modification such as a crack capable of forming a transmission barrier.

The modulus of dynamic elasticity of a normal hardened concrete varies between 200,000 and 600,000 kg/cm². It varies with the actual quality of the aggregates, being higher for concretes with siliceous aggregates than for concretes with limestone. The modulus E_b conforms approximately to the law of mixtures for a relatively compact concrete;

$$E_b=\frac{AE_a+ME_m}{A+M+O}$$

where E_a is the modulus of the aggregate of volume A, E_b is the modulus of the mortar of volume B, O is the volume of the voids.

The order of magnitude of the modulus of a hardened mortar is approximately 200,000 kg/cm², that of a river siliceous aggregate (Seine aggregate) 630,000 kg/cm²; that of quartz 800,000 kg/cm²; for limestone, it varies between 55,000 kg/cm² for very soft limestones to 250,000 kg/cm² for average limestones and 700,000 kg/cm² for very hard limestones such as marbles.

The Poisson's ratio of concrete has received attention in only a few studies [56, 60]. At first we find that for a stress below half the breaking load the transverse deformations are wholly reversible to within the precision of the measurements. Beyond this, irreversible deformations begin to occur which are due in part to microfissuring. It is found that Poisson's ratio varies between 0.10 and 0.30; it is higher as the concrete is younger or less strong. For a hardened concrete, 0.20±0.02 is currently found. By using the dynamic method, we nevertheless obtain a higher ratio, close to 0.30 [60, 61].

Rapid Plastic Deformations

We shall use the term rapid plastic deformations to distinguish such deformations *a priori* from creep produced over a prolonged period. The deformations we are here considering are those that are due to a loading of duration less than 1 hr, a time which corresponds to the practical duration of a loading and unloading experiment in a laboratory. The plastic deformation, moreover, varies little between 1 min and 1 hr in the light of the deformation that subsequently appears in the course of time [62]. In any case, the creep that we shall later consider takes these "instantaneous" deformations into account. This being said, let us examine the curve that represents deformations of this kind in the coordinates T and Δ_P (fig. 17). This curve is concave toward the abscissa, passes through a maximum T_R corresponding to a deformation Δ_R which corresponds to the rupture in the sense usually given to this term, that is to say at the maximum load that the solid can bear. In the course of a test of this kind, it is possible to make a number of supplementary measurements on a fairly slender prism. In addition to the longitudinal and transverse deformations it is possible to place at mid-height a microphone connected to an amplifier and a device capable of recording the sound characteristics, that is to say the sounds that are produced in the concrete under the action of loading. In addition, it is further possible to set up an apparatus for measuring the speed of the shocks along a diameter (normal to the direction of the load applied). The test piece being loaded, the microphone records multiple feeble sounds, and beyond a load T_i very different noises are heard, which are crackings. They increase in frequency and in intensity when the test piece reaches the breaking point (fig. 18). For a load below T_i the speed of sound is constant, and drops beyond this. The crackings are thus indications of internal ruptures that disturb the continuity of the structure. These ruptures have been observed by Berg [63], Freudenthal [82], Rusch, and ourselves. Their length is a few millimeters and their thickness a few microns. The increase in the load augments the density of this cracking and enlarges the cracks which, as they join, lead to rupture.

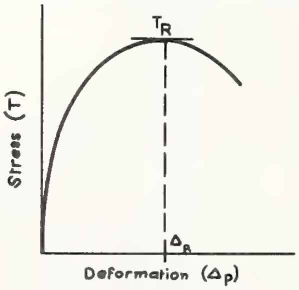

FIGURE 17. *Curve for rapid plastic deformation.*

The transverse swelling is likewise characteristic; Poisson's ratio remains constant up to T_i, then increases to reach 0.5 and beyond shortly before rupture. This transverse swelling appears to be due to the establishment and the dilation of microfissures, the privileged direction of which is parallel to the axis of the compressive stress. To summarize, we see that the rupture properly speaking is preceded by a "pre-rupture" which appears rather early, between 50 and 75 percent of the standard breaking load. What we then measure is no longer a simple plastic deformation since there is added to it the effect of a disorganization.

In general, it seems that no measurable instantaneous plastic deformation is found in compression below ½₀ of the breaking load. Here are a few figures obtained by Le Camus:

$\frac{T}{T_R}$	0. 05	0. 10	0. 20	0. 30	0. 50
$\frac{\Delta_R}{\Delta_E}$	0	0. 10	0. 18	0. 22	0. 26

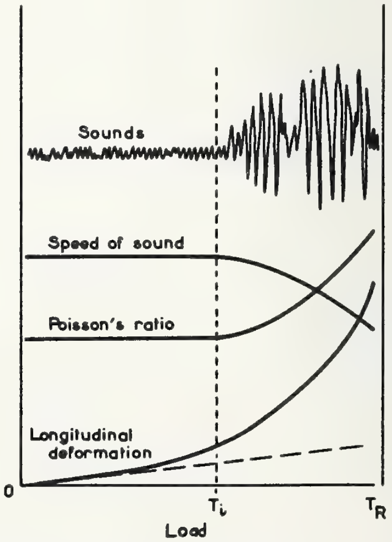

FIGURE 18. *Changes in mechanical and sound characteristics on loading.*

Glanville [41] has given deformation curves of concrete under loads maintained for variable periods from 5 to 60 seconds on a concrete containing 350 kg of portland cement per m^3, loaded at 28 days. The plastic deformation increases with time. At about 30 percent of the breaking load, $\frac{\Delta_R}{\Delta_E}=5$ percent at 15 sec, 10 percent at 30 sec, and 15 percent at 60 sec.

Deformation under heavy loads has been specially studied by Shank [64]. His paper appears to lend itself to the interpretation provided by the following table for measurements at 1 hr:

$\frac{T}{T_R}$	0.855	0.88	0.905
$\frac{\Delta_R}{\Delta_E}$	0.30	0.45	0.55

For $\frac{T_E}{T_R}=92$ percent the rupture occurs before 1 hr. It occurs at 7 hr for $\frac{T_E}{T_R}=0.905$. The author proposes representing the rapid plastic deformation in the form $\Delta_R=cT^{1/n}$. We may mention that Blakey [65] proposes an expression $T=E\Delta e^{-\Delta/\Delta_m}$ where Δ_m is the deformation at the maximum of the curve. Smith and Young [66] propose the formula: $\frac{T}{T_R}=\frac{\Delta}{\Delta_m}e^{1-\Delta/\Delta_m}$.

But finally, it must be confessed that we do not know a great deal about rapid plastic deformation in terms of the age, the curing medium, etc. We know only that it is less than the elastic deformation and negligible up to 10 percent of rupture. As for the plastic Poisson's ratio, we know practically nothing about it.

In tension, rapid plastic deformation tests are few in number. Our tests and those of Grassam and Fisher [67] indicate a total linear deformation up to 85 percent of the breaking load in tension, with the plastic deformation preceding rupture not exceeding 8 percent of the elastic deformation. Todd [68] on the contrary indicates a few experiments in which the plastic elongation obtained beyond 75 percent of the tensile strength exceeds a quarter of the elastic deformation. These involve prisms containing a longitudinal steel bar, however, and it is recognized that the rupture or cracking elongation of a concrete is increased in the proximity of a reinforcement. As sudden cracking cannot occur, it is replaced by a microfissuring that may look like plastic deformation. In order to check this, we have used a device composed of a tube of steel within which concrete was poured [31, 62], an inside thread ensuring adherence between the two. The tensile stress was applied to the tube by means of threaded sleeves. Under these conditions the tube stretched, along with the concrete, to the same amount. The elongation Δ was measured on the outside of the steel tube, in the central area, by means of strain gages. If Ω_a is the section of the tube having a modulus of elasticity E_a and Ω_b the section of the concrete having a modulus of elasticity E_b, the stress must be $F=\Delta(E_a\Omega_a+E_b\Omega_b)$. The curve that represents the relation $F(\Delta)$ must be included between two straight lines of inclinations $\frac{F}{\Delta}=E_a\Omega_a+E_b\Omega_b$ (a perfectly elastic system) and $\frac{F}{\Delta}=E_a\Omega_a$ (the concrete no longer reacts, it is broken, fig. 19). We find that the experimental form is OAB. It is identical with the upper straight line as far as A, then bends. If there were a sudden break at a given moment, we should find a drop CC′, and the reaction of the concrete should instantly be equal to zero. Yet not only is there no sudden break, but the reaction of the concrete does not become equal to zero. This result may suggest plasticity, but in order to decide the matter another experiment was indicated. This time the concrete was not bound to the tube except at its extremities; it was separated from it by a sheath of foam rubber. The CC′ reactions of the concrete were then the same up to A, then less, equaling zero shortly thereafter, but this time also without suddenness. If we record both types of reactions $F_R=CC'$ in figure 20 we see that the maximum reaction of the free concrete, that is to say its strength, occurs near A and equals zero shortly thereafter as soon as cracking has crossed the section. For concrete supplied with a steel guide the reaction in M′ is greater than in M.

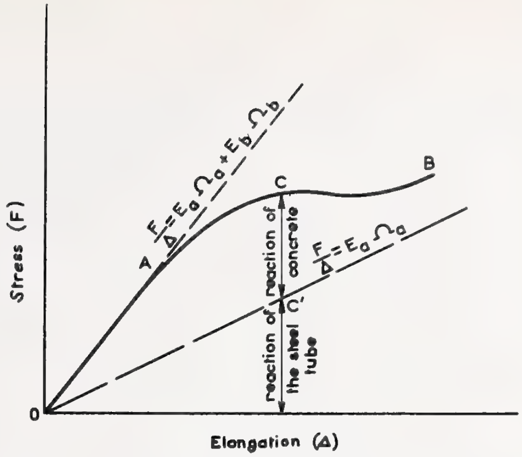

FIGURE 19. *Elongation of concrete in a threaded steel tube.*

All this shows that the apparent plasticity of concrete in tension is improved by the presence of a reinforcement.

Tests of the plasticity of concrete have been made by bending, strain gauges being placed on the strained surface of joists poured without reinforcement. On neat paste, at 3 months, our tests showed that up to 90 percent of the breaking load no measurable residual deformation occurs. At 95 percent of this load, the plastic deformation

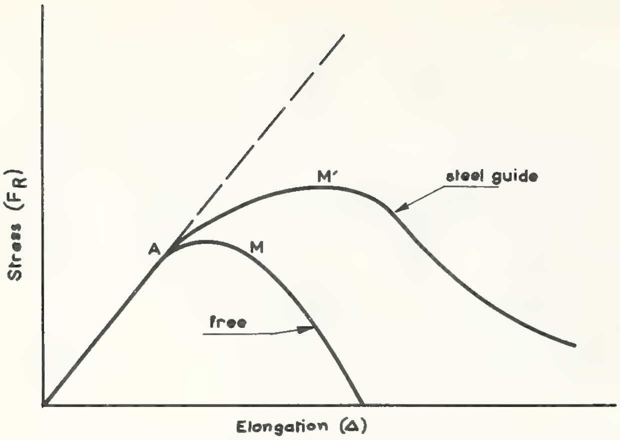

Figure 20. *Behavior of concrete unrestrained in a steel tube compared with that in a threaded tube.*

was 2 to 5 percent of the elastic deformation at 1 hr and 6 to 11 percent at 4 hr. The few experiments made in torsion [56] seem to show that plastic deformation appears earlier than in tension; close to rupture $\left(\frac{T}{T_R}=0.9\right)$ it amounts to 10 percent of the elastic deformations, but it is possible that errors due to the friction of the supports may account for this figure. Such measurements should be undertaken on tubes.

Creep—Slow Plastic Deformations

When concrete, after having been loaded, remains under the influence of this load over a long period, it continues to become deformed. It is this slow plastic deformation that we call creep. It appears to approach a limit to the extent to which the load is maintained constant for a very long period. We say that it appears to approach a limit without being really able to affirm this. The tests begun by R. Davis [69] some 30 yr ago have not yet brought out this stabilization. Creep in 1 yr being taken as a unit, it becomes after 2 yr 1.14, after 5 yr 1.20, after 10 yr 1.26, after 20 yr 1.33 and after 30 yr 1.36. These are the longest tests known; no one knows what happens to the concrete at the end of 100 yr, and there is no chance of my finding out. I therefore suggest that Davis' measurements be carefully continued by his successors in order that our scientific heirs may some day be able to settle this important point. To build a sealed room where the atmosphere is fixed at 50 percent humidity and into which one will enter religiously every 20 yr does not appear to me to constitute an expense incompatible with the financial means used in other fields for scientific research in a country like the United States of America.

Having said this, let us remove a load from a test piece after a time *t*. The test piece becomes deformed in the opposite sense instantaneously, then it continues to be deformed for a certain time (fig. 21). Without concluding as to whether what we have is a deferred elasticity or a reaction of the elastic aggregates on the plastic phase that the binder may constitute, we shall say that, finally, a permanent deformation remains. But this includes in part the shrinkage that the concrete would have undergone during the same period. The permanent deformation, the one due to creep, which is a consequence of the applied load, thus appears to be the difference between the permanent deformation and the shrinkage.

If at the moment $t' > t$ the creep test piece and the shrinkage test piece are both placed in water, they swell. The test piece that has been subjected to a load swells more than the one that was cured without load and more markedly so to the extent to which the load applied has been greater.

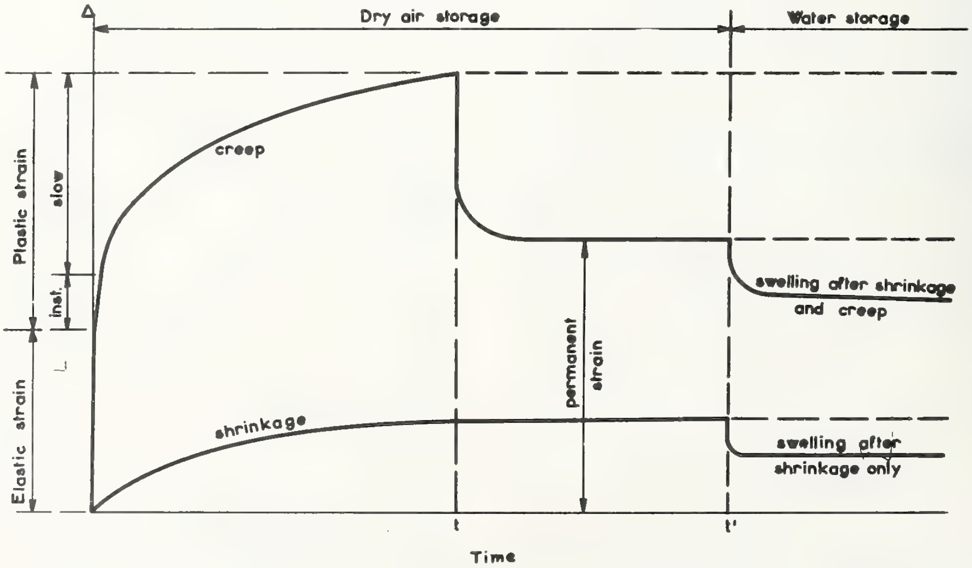

Figure 21. *Creep and shrinkage as affected by conditions of loading and storage.*

Such are the rough outlines of the phenomenon that we shall examine in detail. The first known study of creep is the one published by Woolson in 1905 [70]. We shall mention further, among the precursors, W. K. Hatt in 1907, E. Freyssinet in 1907, F. R. McMillan in 1915. A fairly complete bibliography will be found in the paper presented before the Munich symposium in 1958 [62.]

Creep in Compression

Most creep curves in terms of time have an asymptotic shape; they appear, under constant load and other things being equal, to show an increase in deformation Δ toward a limit value which can be reached after several dozen years. In any case the magnitude $\frac{d\Delta}{dt}$ has a decreasing value with t. Many authors have tried to give an empirical form to the curves obtained. Lorman [71] gives the function $\Delta(t)=T\frac{mt}{n+t}$ in which m and n are two constants. The final value of the creep is thus $\Delta=mT$ where m is called ratio of creep and T the applied stress. There is found the concept of period, the time at the end of which Δ reaches half its final value Δ_m, this time being $t=n$.

We may note that this expression can be written in the differential form:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{1}{n+t}.$$

Lee [72] gives a differential expression:

$$\Delta=\Delta_m[1-e^{-F(t)}]$$

whence:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{dF(t)}{dt}.$$

Ross [73] uses a simple rheological model and gives:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)K$$

a simple equation of viscosity. Torroja and Paez [74] use a more complete model with springs, dashpots, and dry friction in parallel and in series. It is difficult to derive a simple general equation from it. Freudenthal and Roll [83] also use a rheological model which leads to an expression:

$$\Delta=C\left[1-e^{-\frac{t}{t_m}}\right]+T\alpha\left[2-e^{-\frac{t}{t_1}}-e^{-\frac{10t}{t_2}}\right].$$

t_m, t_1, and t_2 are the times of relaxation of three visco-elastoplastic systems considered. α and C are constants characteristic of the solid, and T is the applied load. There is therefore a term independent of the load which represents shrinkage, creep properly speaking being the sum of two viscous deformations. McHenry [75] gives a relation composed of two exponentials:

$$\Delta=\alpha(1-e^{-rt})+\beta e^{-pa}(1-e^{-mt})$$

where a is the age of loading, α, β, r, m, and p constants. What we have is the superposition of two different creeps $\Delta_1+\Delta_2=\Delta$, both simply viscous, so that:

$$\frac{d\Delta}{dt}=\frac{d\Delta_1}{dt}+\frac{d\Delta_2}{dt}=(\Delta_{m_1}-\Delta_1)K_1+(\Delta_{m_2}-\Delta_2)K_2(a)$$

Thomas [76] proposes an equation $\frac{d\Delta}{dt}=\frac{A}{(B+t)^n}$ which also leads to an exponential form of Δ. All authors, however, have not accepted the assumption of limited creep, and Straub [77] in particular indicates the relation $\Delta=Kt^{1/n}$, a purely logarithmic form. We shall not endorse this proposal which if need be can represent the beginning of creep but which does not seem able to maintain itself indefinitely, and we shall come back to the simple equation:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{dF}{dt}$$

although for very young concretes, Delarue [78] believes it is necessary to add a term of consolidation of form $\frac{A}{\sqrt{t}}$ which would tend toward a finite limit after a few days. It appears not impossible to introduce such an influence into the function F, however, for if one takes into account the form of the deformation curve there is nothing to prevent looking for its derivatives. Finally, it is convenient and probably correct to represent creep by an equation stating that the speed of deformation at a given moment is proportional to the deformation that remains to be accomplished and to a function $\Phi(t)=\frac{dF}{dt}$ which takes into account the state of the concrete at the moment considered. If we set aside the instantaneous plastic deformation $t>1$ hr, we find that Φ is the sum of a constant and of a function of time, or $\Phi=K_1(a,t)+K_2$ where a is the age of loading from the beginning of setting. For concretes loaded beyond 1 week, it appears that:

$$K_1(a,t)\simeq\frac{K_1}{a+t}$$

or $\frac{d\Delta}{dt}=(\Delta_m-\Delta)\left(\frac{K_1}{a+t}+K_2\right)$ when the applied load is less than half the breaking load, the usual area of use of concrete.

This leads us to write:

$$\Delta=\Delta_m\left[1-e^{-\left(K_1\log\frac{a+t}{a}+K_2t\right)}\right]$$

and

$$\log\frac{\Delta_m-\Delta}{\Delta_m}=-\left[K_1\log\frac{a+t}{a}+K_2t\right].$$

If we set down $\log \frac{\Delta_m - \Delta}{\Delta_m}$ as ordinates and $\log \frac{a+t}{a}$ as abscissas, we get a diagram like that in figure 22. The curve is tangential and for a long time close to the straight line

$$\log \frac{\Delta_m - \Delta}{\Delta_m} = -K \log \frac{a+t}{a}$$

from which it subsequently separates [62]. This allows calculation of K_1 and K_2. We have found for a series of concretes that K_1 is in general between 0.60 and 0.80 and K_2 between 0.0005 and 0.0015, much lower than K_1.

We shall see further that it is possible to have a different conception of shrinkage in which it is possible to separate basic creep from a deformation favored by the movement of water.

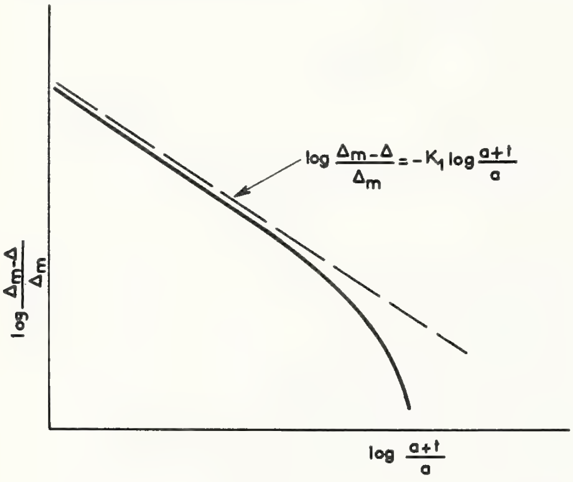

FIGURE 22. *Relation of* $\frac{\Delta_m - \Delta}{\Delta_m}$ *to* $\frac{a+t}{a}$.

Size of Load

Certain authors claim that the final deformation of a concrete, after prolonged creep under constant external conditions, is proportional to the load: Glanville [41], L'Hermite [31], Mamillan [84], Neville [85], etc. Others appear to be certain of the contrary: de la Peña [86], etc.

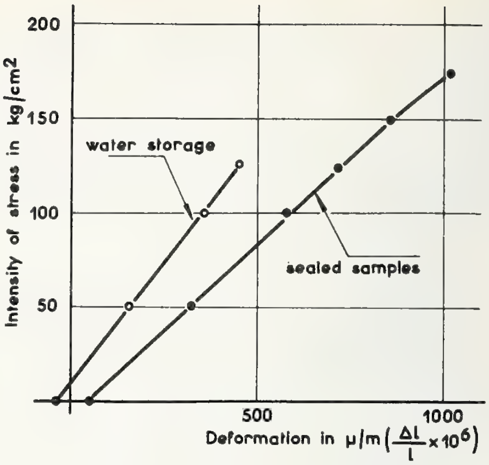

FIGURE 23. *Portland cement concrete loaded at 28 days; creep measured 70 days after loading (shrinkage or swelling included).*

Our experiments have shown an almost perfect proportionality for samples cured in such a way that there can be no exchange of water with the outside up to 50 percent of the breaking load. The same holds for concretes cured in water (fig. 23). On the other hand, for curing in dry air, the linearity appears less clearcut (fig. 24). However, it can be allowed that below 100 kg/cm^2, or one-third of the breaking load, the creep, deducting shrinkage, is proportional to the applied load to within less than 10 percent.

Certain tests suggest that the total deformation becomes linear and proportional to the load, shrinkage included, when the influence of the latter, considerable for slight loads, becomes negligible for higher pressures [62] (fig. 25). But in view of the slight deviation that this involves in relation to linearity, it seems that the latter can be considered as practically acceptable for engineering calculations for an intensity of stress below 50 percent of the breaking limit.

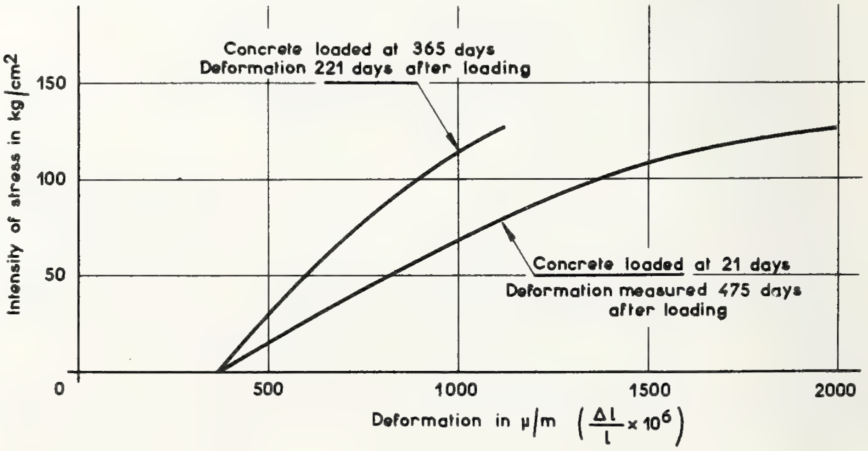

FIGURE 24. *Creep at 50 percent rh.*

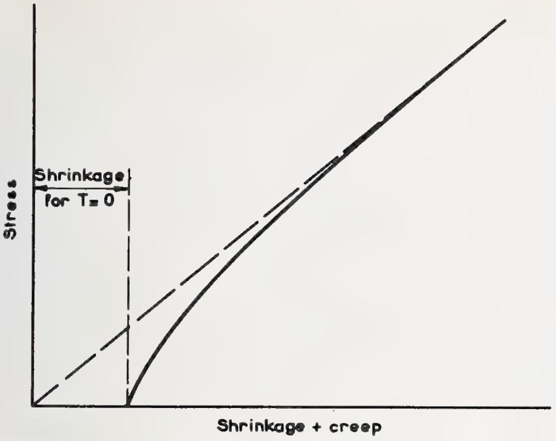

FIGURE 25. *Deformation, including shrinkage, in relation to stress.*

Age of Concrete at the Moment of Loading

Experiments made on this subject are relatively few in number when great differences in age are involved. What is certain, in any case, is that the creep after several years of loading is less as the age at which the loading has been effected is more advanced.

Let us call $\Delta_n(7)$ the creep after several years of a concrete loaded at 7 days and $\Delta_n(a)$ the creep after an equally long time of a concrete loaded at the same rate at any age a. The relation $\frac{\Delta_n(a)}{\Delta_n(7)}$ is a decreasing function. Figure 26, drawn from the results of experiments of which we have had knowledge and of experiments which we have carried out, shows that, aside from the scatter, the relation $\frac{\Delta_n(a)}{\Delta_n(7)}$ diminishes in a practically linear way with the logarithm of the age. It seems that this must approach a limit, but nothing in the data at present available allows us to establish it. It is believed that the total creep deformation varies inversely with the mechanical strength of the concrete at the time of loading, but the precise form of this relation remains to be found.

Mode of Curing

Davis [69] was the first to bring out the important influence of the humidity of the curing medium on creep. By way of example, we may indicate that after 1,600 days the following creeps were obtained on a portland cement concrete loaded at 28 days at 65 kg/cm^2:

Relative humidity	Total creep	Shrinkage without load	Calculated creep
	μ/m	μ/m	μ/m
Water	180	−120	200
Air 99 percent	250	−100	240
Air 70 percent	1, 450	+750	1, 460
Air 50 percent	2, 100	+1, 200	2, 100

We observe the enormous influence of the humidity. The interdependence or at least the correlation between creep and shrinkage appears positive. We have proposed [31] relating these two phenomena by a formula:

$$\Delta_m = \Delta_{mi}(1 + Q\Delta_r)$$

where Δ_{mi} is the creep in the absence of shrinkage, Q a constant depending on the concrete and Δ_r the shrinkage with the corresponding humidity. This relationship indicates that creep in a constant atmosphere is a linear variable of the absolute shrinkage measured in relation to the swelling curve. The fourth column of the preceding table gives the result of the calculation which indicates a good correlation.

The mode of curing that precedes loading likewise has a great influence. R. Davis has shown that curing in water before loading may greatly diminish the outer creep. Curing in water for 28 days instead of in dry air (50 percent rh) reduces the creep (shrinkage being deducted) from 550 to 175 μ/m at 350 days. It is possible to bring in the mechanical strength R reached at the moment of loading and to add a correcting term to the empirical formula already established:

$$\Delta_m = \Delta_{mi}(1 + Q\Delta_r)f(R)$$

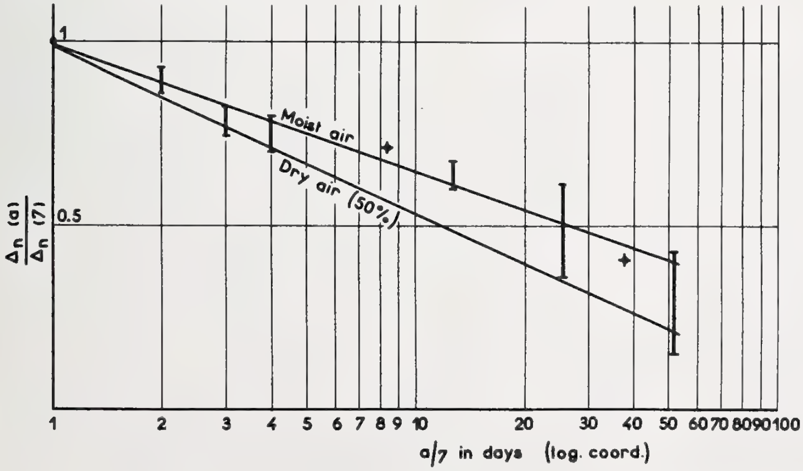

FIGURE 26. *Variation of creep in terms of age of loading.*

where $f(R)$ is a variable to be determined; for instance as a first approximation $f(R)=A/R$.

But an unexpected phenomenon was brought out at the last RILEM symposium in Munich (Oct. 1958): "alternations of humidification and of drying produce an increase in creep". In order to check this fact, we used a certain number of samples having stood for 600 days in dry air under a series of permanent loads: 0, 50, 100, 150, 200 kg/cm^2. We then placed them in water. Some swelled, others continued to contract; but the absolute difference between the swelling of the nonloaded control and the deformation under load was positive and spectacular. For 28 days, the creep of the sample exposed to a compression of 150 kg/cm^2 was 300 μ/m (figs. 27 and 28). After this period, the test pieces, still loaded, were replaced in dry air for 70 days. We then witnessed a general shrinkage, independent of the load but without creep, properly speaking. Next, the samples were again placed in water for 90 days: there was again creep amounting to approximately 180 μ/m per 150 kg/cm^2. A fresh exposure to dry air for 28 days gave rise only to a shrinkage independent of the load. These unsystematic experiments, which must be considered merely as a first attempt, appear to show that creep as it is usually considered—the difference between shrinkage and deformation—increases rapidly through humidification and remains stable during subsequent drying. Similar results were likewise obtained by Hansen [87]. It is possible, however, to consider another aspect of the phenomenon as it is indicated by figure 27. Without load, the concrete swells in water, shrinks in dry air, and so forth. Under load, the swelling is reduced and varies inversely with the compressive load. It may be said that under a pressure p equal to 100 kg/cm^2 in the case considered, the swelling in water is compensated. It is not far from this conception to that of swelling pressure put forward by certain authors, including Powers. In any case, it would be interesting to pursue investigations of this kind.

Tests by Seaman [88] have borne on the influence of the preliminary treatment of concrete by steam. The treatment in autoclave at 180 °C under steam pressure gives a modulus of elasticity 30 percent lower than that of a concrete hardened in moist air at 30 °C. But at 70 days, the creep of the treated concrete is approximately one-quarter that of the other. Moreover, it seems that this creep is very rapidly stabilized (in approximately 30 days). When one tries the silico-calcareous reaction with introduction of powdered silica, the creep becomes very slight after treatment, namely 50 μ/m at 90 days, and is stabilized after 2 weeks. This diminution of the deformation corresponds to that of shrinkage. There is probably a relation with the structure of the hydrates.

We call attention also to Ross's original article [89] in which he proposes treating the concrete before loading by heat and vacuum in order to produce a rapid drying. Placing in a damper atmosphere at the moment of loading determines a swelling that at least partly compensates the subsequent creep.

The influence of temperature on creep has been studied by Serafim [90], who indicates that this factor is appreciable in the first days of loading (4 to 7 days); afterwards the deformation curve remains parallel. The difference for 45 °C that persists to 60 days under a load of 25 kg/cm^2 applied at 8 days of age without exchange of water with the outside (coated test pieces) is 160 μ/m as against 400 μ/m of total creep at 20 °C.

Composition of the Concrete

The effect of the cement content has been studied by Davis, Glanville, and others. The grain size plays a role as well as the water/cement ratio. We find upon examination of these test results that there is a lessening of creep when the cement content increases; a lessening compensated by the increase in shrinkage. However, it is possible to observe a new increase for rich mortars, and beyond question a considerable creep for neat pastes. This seems to mean that there is a concrete composition with minimum creep which is likely to be found with an aggregate having a special mineralogical composition (quartz or very hard limestone) and for a rather high cement content, which it would be presumptuous to try to specify at this point but which must take into account the grain size of the aggregates and the nature of the cement. The influence of the nature of the aggregates is in fact really appreciable when their modulus of elasticity is very low or when they can be subjected to actual plastic deformations. The tests made by Davis [69] give the following creep values (shrinkage included) at 25 yr for 50 percent rh; sandstone, 2,600 μ/m; basalt, 2,100 μ/m; granite, 1,700 μ/m; and quartz, 1,300 μ/m. He also indicates that creep increases especially at the beginning when the size of the aggregates increases. Kordina [91] produced eight concretes of identical cement content with different aggregates. He obtained two families of concretes: the one includes aggregates of the following types: siliceous gravel, quartz, marble, granite and basalt; the other includes the sandstones. After 1 yr of curing at 65 percent rh, the first family gives a specific creep in relation to 1 kg/cm^2 which varies between 1.7 and 2.3 $\times 10^{-6}$; the second family gives a creep which varies between 6 and 7×10^{-6}. We may note further that the creep increases only slightly but in a manner corresponding to the water/cement ratio, approximately following the concomitant variations of shrinkage without load.

The influence of the nature of the binder has been studied by Neville [85, 92]. It appears that, generally speaking, shrinkage under a given load diminishes when the strength of the cement increases (the creep under this constant load

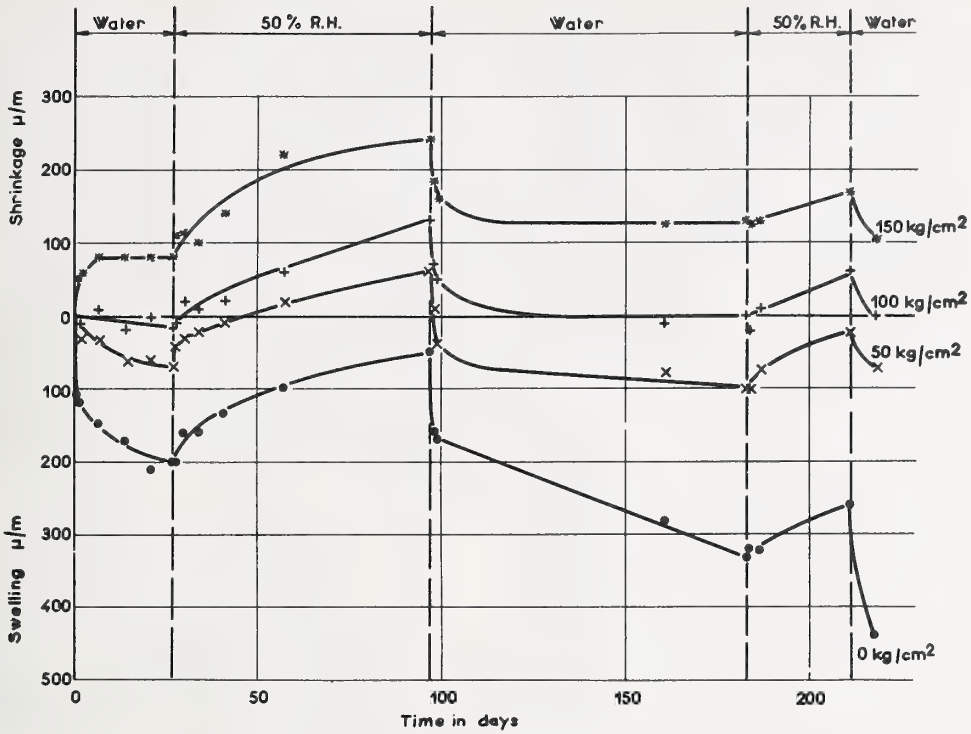

FIGURE 27. *Deformations due to alternations in humidity in relation to the deformations of test pieces loaded under the same stresses and cured continuously at 50 percent rh.*

Series loaded at 7 days. Initial recording at first placing in water after 600 days of loading. Creep at this time:

0 kg/cm²: 280 μ/m
50 kg/cm²: 1,000 μ/m
100 kg/cm²: 1,800 μ/m
150 kg/cm²: 2,900 μ/m

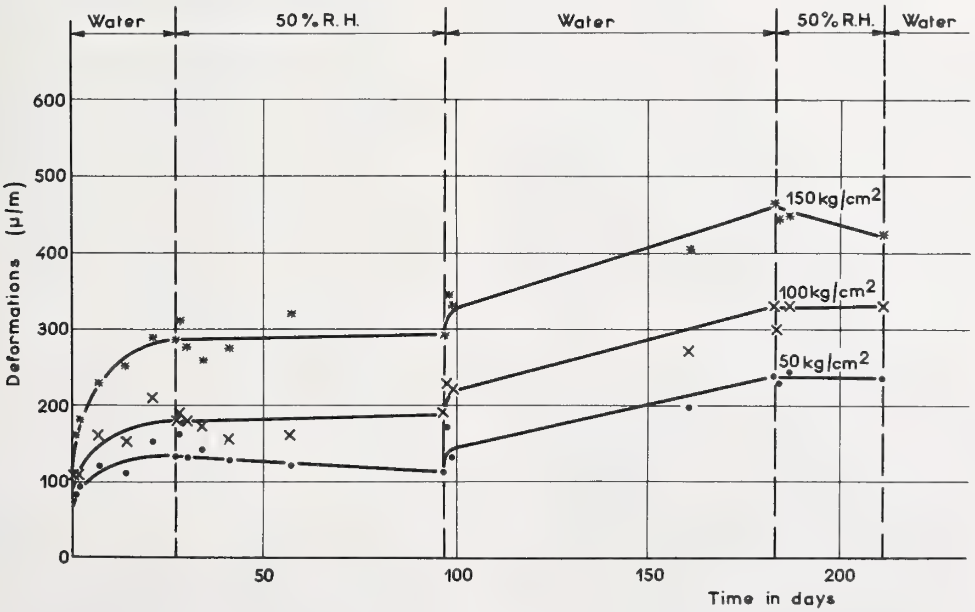

FIGURE 28. *Increase in creep in relation to the nonloaded test piece.*

being, moreover, inversely proportional to the strength). The author indicates further that aluminous cement has a lower creep than portland, that creep increases with the fineness at the same time as the shrinkage. The influence of the chemical composition of the clinker has not yet been studied and is a subject well worth looking into. Indeed certain works like prestressed concrete bridges require a concrete having low creep, whereas works such as gravity dams where the structure must adapt itself to the movement of the foundations should use concretes with a relatively higher creep. The adaptation of the binder and the composition to the liability to plastic deformation seems to be a problem of construction that has not yet been sufficiently considered.

The Influence of Volume

The dimensions of the test piece have a bearing on the speed of creep and perhaps also on its final value. Davis' tests [69] show at 10 yr creeps that decrease with the dimension for curing in air. Gwosdew [93] has studied prisms whose dimension ranged from 1 to 8. For an intensity of stress equal to one-half the breaking load, the creep after a few years was approximately three times greater for the small test piece than for the large one. Results of the same kind were obtained by Karapetian [79]. The Russian school advocates the use of the parameter $\tau = t\left(\frac{K}{D}\right)^2$ by analogy with what has been indicated above for shrinkage.

However, it appears certain that for concretes cured within a membrane preventing any exchange of water with the outside, creep is independent of the dimensions. The supplementary creep that accompanies drying occurs after a period proportional to $\left(\frac{R}{K}\right)^u$ where u varies between 1 and 2, so that the parameter τ which defines the time of equal creep must be of the form $\tau = t\left[a + b\left(\frac{K}{R}\right)^u\right]$ with u included between 1 and 2. However this may be, it is indispensable that in experiments relative to the influence of the dimensional scale on shrinkage, comparisons should be made with the adiabatic shrinkage or basic shrinkage, in the absence of evaporation or water absorption. Only under these conditions can useful comparisons be obtained.

Effect of Load Removal

When the load is removed from a test piece that has been placed for some time under a permanent load, it undergoes a partial instantaneous recovery, followed by a further deferred recovery, during a visco-elastic period, that augments the instantaneous elastic recovery by 15 to 30 percent (fig. 21). The magnitude involved is thus appreciable.

When the recovery is effected in the same medium as the loading, the phenomenon appears to be markedly viscous, for it corresponds to an equation $\Delta = \Delta_v(1 - e^{-Qt})$ where Δ_v is the total recovery and Q a constant. Representation with the coordinates log $(\Delta_v - \Delta)$ and t gives straight lines (fig. 29).

The question arises as to what this recovery is due to: perhaps to a reabsorption of water from the surrounding air, but the measurements of weight that we have made have been absolutely negative (if there is recovery of weight, it is negligible); perhaps to a movement of the water in the hydrated phase; perhaps again to a reaction of the elastic aggregate phase on the viscous hydrated-cement phase (this last assumption appears the most probable).

McHenry [75] gives a hypothesis on the reversibility of creep (fig. 30). Let us consider a creep curve obtained after age a_1: curve A. Let us now consider a creep curve after age a_2: curve B. If we unload test piece A, the unloading curve after time a_2 is obtained by subtracting from the

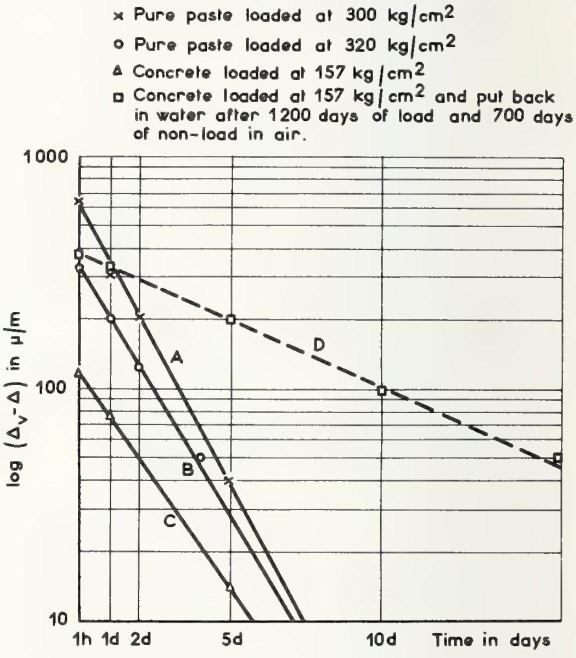

FIGURE 29. *Elastic aftereffect.*

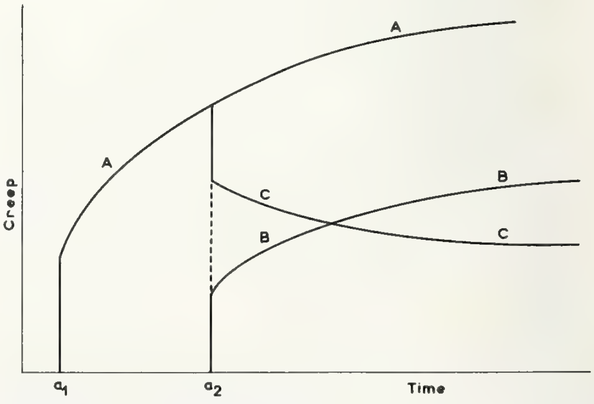

FIGURE 30. *Representation of the hypothesis on the reversibility of creep.*

ordinates of curve A those of curve B, to form C. This hypothesis is attractive in its simplicity, and it appears to have been verified in several cases [94]. We have observed that it gives an acceptable approximation for some 50 days at a maximum when the creep occurs in water but that it remains uncertain for creep in dry air ($\theta = 50\%$). The postelastic effect is rapid and viscous, whereas creep does not conform to a simple law of viscosity. It may be said, however, that McHenry's hypothesis is a convenient approximation.

We may say further that if the concrete is placed in water after removal of the load, it swells more than a test piece that has never been loaded placed under the same conditions, and all the more as the load applied has been greater (fig. 31). But, the weight measurements do not on this account appear to indicate an increased reabsorption of water. It is also to be observed that this swelling appears only if the load applied exceeds a certain magnitude (in the case of figure 31, above 45 kg/cm^2). This is a very puzzling phenomenon and invites further scrutiny. Figure 32 shows the changes in length of a concrete and indicates in particular that the residual deformation after unloading and placing in water is much less than the maximum deformation. It will likewise be observed that if placing in water under load gives rise to an increase in creep, the placing in water after unloading gives rise, on the contrary, to a higher elastic recovery. I should like to see this lead to a few experiments such as, for example, the reloading at the moment of placing in water to compare it with the effect of unloading. This procedure might give indications as to the influence of water on viscosity and an estimate of the forces of elastic recovery.

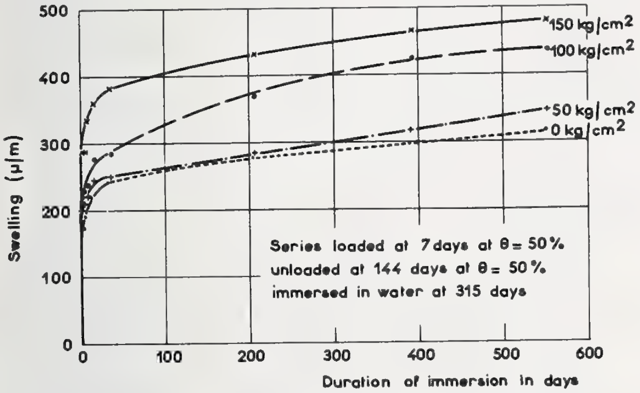

FIGURE 31. *Swelling due to water immersion after unloading.*

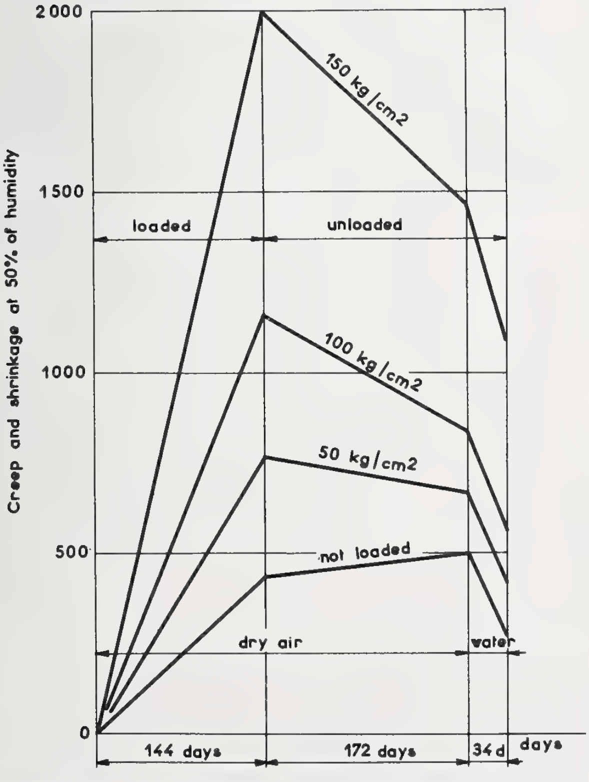

FIGURE 32. *Deformation of a concrete loaded at 7 days unloaded at 144 days, and submerged at 316 days.*

Transverse Deformation of Concrete (Poisson's ratio)

We have noted that under instantaneous loadings the reversible transverse deformation was 10 to 30 percent of the longitudinal deformation and that this ratio diminishes with age. If we call $\sigma_p = \frac{\Delta'_p}{\Delta_p}$ the ratio of the longitudinal and transverse plastic deformations, we call this "the plastic Poisson's ratio". Certain authors consider it to be equal to 0 or in any case much lower than Poisson's ratio relative to elastic deformations. This conclusion is at all events in contradiction with the classical theory of plasticity which indicates $\sigma_p = 0.5$, showing thereby that plasticity is a phenomenon which occurs without change in volume. Our tests made recently and very carefully to clarify this question have shown the existence of a plastic Poisson's ratio very close to or equal to the purely plastic Poisson's ratio for instantaneous deformations (fig. 33). Up to 200 days, this ratio appears to hold, making allowance for shrinkage, which incidentally is not always the same per unit of length along the axis and the side of a prism. In our experiments we have found it close to 0.2 (Mamillan, to be published in the Annales de l'Institut Technique du Bâtiment et des Travaux Publics). Kordina [91] has found Poisson's ratio varying with the various types of aggregates. For rolled quartz and basalt he obtains a value close to 0.30, for river siliceous aggregates, granite, and crushed quartz, the values are grouped around 0.20, and, finally, for sandstone the Poisson's ratio becomes less.

It therefore seems that creep does occur with a lessening in volume and is governed by the elastic skeleton. If this hypothesis is confirmed the conclusion is of great interest, for it would make it possible to relate the transverse deformation to the longitudinal deformation in a biunivocal way.

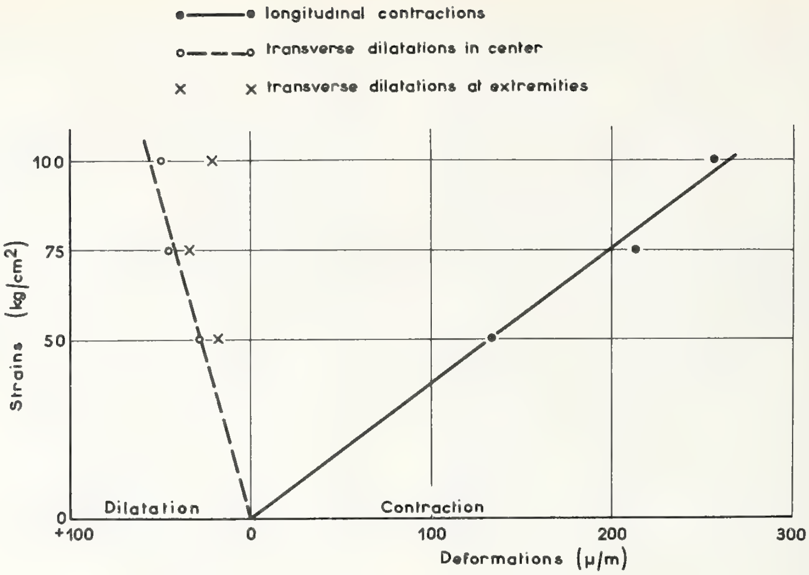

FIGURE 33. *Instantaneous deformations of test pieces.*

Curing: 50 percent rh.
Age of loading: 30 days.

However this may be, creep occurs with a lessening in volume, which appears undeniable, and if this phenomenon is produced by the displacement of a viscous phase it cannot occur without an increase in compactness. Apparently this increase exists and must be confirmed by experiments on strength. Washa and Fluck [95] have operated for more than 10 yr and have shown that at the present date the increase does not exceed 5 percent of that of the nonloaded control concretes. On the other hand, the modulus of elasticity increases from 20 to 30 percent between the nonloaded test pieces and the loaded ones. This result appears to be confirmed by R. Davis' tests (verbal communication). Finally, while one cannot anticipate an appreciable increase in strengths as a result of creep, the increases that are observed below 50 percent of the breaking limit are *always* positive and clearly show the effect of an increase in compactness.

Creep Under Repeated Loads

If instead of leaving a permanent load resting on the test piece one repeats the same load at a rather rapid rate (several times per minute), one observes an acceleration in plastic deformation. Tests have been made by Le Camus [56] on two groups of identical test pieces. One of these was subjected to a permanent compressive stress of 126 kg/cm² and the other to the same load repeated at a rate of 500 times per minute. After 24 hr of treatment (720,000 repetitions), the permanent deformation observed was the same as for 28 days of permanent load. After 3,600,000 repetitions (5 days) the effect was identical with that of 180 days of static load. After 10 million repeated loadings the deformation was the same as that resulting from 600 days of permanent load.

We wanted to find out if a concrete already deformed by creep was sensitive to the effect of repeated loads in order to ascertain whether the deformation by repeated load was of the same nature as deformation under permanent load. (We already knew that it was not produced by microfissuring for the transverse modulus of elasticity had not been lowered in the course of the treatment). Thus a test piece loaded for 1,000 days was unloaded, placed at rest, and reloaded under repeated stresses. At the end of 3 million repetitions the plastic deformation had increased by a maximum of 6 percent.

Creep under permanent load and plastic deformation under repeated load do not have a cumulative action. A concrete adapted under permanent load is no longer apt to be deformed under repeated load (if we neglect the 6 percent indicated above which perhaps is due to shrinkage resulting from heating through mechanical hysteresis).

Creep in Tension and in Torsion—Combined Stresses

Tension creep devices are more difficult to make than those for compression. The laws, however, appear to be similar. There is a continuity between elastic and plastic deformations. As the tensile strength is very low as compared to the compressive strength, however, the creep that it is possible to measure is very slight and is limited by rupture to a short time.

It is possible to see that the creep is proportional to the applied load, but it appears at least that the creep is more rapid, and because of this in a bent beam the neutral fiber rises toward the compressed surface and subsequently descends again. We may recall in this connection the tests by Bingham and Reiner [96] on cement joists 1 in. on the side and 34 in. in length subjected to a bending moment. The deformation curve in relation to time has at the outset the form of a parabola and then becomes linear in relation to time; the speed of creep becomes constant. The tests were ended too soon to bring out the possible stabilization and the hygrometric conditions were not well defined.

The simplest combination of stresses is provided by torsion which is a combination of tension and of compression at 90°. The only experiments of this kind that I have come across are those that were carried out in my laboratory by Le Camus [56]. The method has the advantage of eliminating shrinkage, since the latter can apparently not produce a torsion. Tests carried out over 400 days showed that the permanent deformation is proportional to the applied couple. Another observation not devoid of interest is that the shrinkage along the axis is the same for the loaded and the nonloaded test pieces. This identical shrinkage can occur only if the tensile and compressive creeps compensate each other exactly for equal loads of contrary sign.

Dukes and Davis [97] have carried out creep tests on compressed cylinders subjected to a lateral stress. The longitudinal creep deformation measured after 3 months of loading in a damp medium is approximately proportional to the difference in the chief stresses, a result which appears to extend the application of the linear law of deformation. Poisson's ratio, according to the authors, appears to be of the order of 1/6, but the interpretation of the tests is difficult in this case.

Ross [98] has carried out very interesting tests in the case of creep under double stresses. Square test pieces left free in the direction normal to their plane were stressed on the other two pairs of sides. The author believes that from this test could be deduced the linearity of deformation in relation to load and a very low value of the plastic Poisson's ratio.

Theories and Conclusions on Creep

Theories on creep are numerous and varied if not contradictory, which is characteristic of a young science. Some of these theories are simply explanatory or phenomenological; others are quantitative and are aimed at permitting calculation and extrapolation for the needs of builders. As it is difficult to summarize them all and in any case impossible to bring them all together in this report, we shall examine their main features in what is to follow, and we shall begin by asking a few questions.

Where does creep have its seat?

Concrete is composed of two essential parts: a skeleton of aggregates and a phase composed of a more or less hydrated cement with generally an excess of water. The aggregates are in most cases much more rigid than the binding phase and have little susceptibility to plastic deformation. Creep thus appears to have its seat in this binding phase and in its bond with the aggregates.

Why and how does the cement paste creep?

According to certain authors the binding paste is a gel, hence a viscous body, but in continual evolution by virtue of hydration, hence of variable viscosity. Under these conditions, the effect of external forces is to put this gel into movement in such a way that it fills the voids in the concrete. The elastic skeleton follows the movement in the direction of the forces applied with the transverse deformations that are peculiar to it, which conforms to the conservation of the elastic Poisson's ratio observed by different authors insofar as creep is concerned.

According to other authors, the binding paste is composed of a padding of crystals forming no longer a viscous body but a plastic solid with a deformation which is viscous, to be sure, but having cohesion and rigidity, these two characteristics evolving with the degree of hydration. It is possible, for that matter, that the two forms of binding paste coexist, the proportion of the second in relation to the first increasing with time according to conditions of hydration.

Can several forms of creep be distinguished?

In this case there would have to be an indefinite viscous creep and a limited plastic creep.

Viscous creep must be in part reversible upon unloading by virtue of its association with an elastic skeleton. And unloading does have a character of viscosity (fig. 29).

Plastic creep cannot be reversible upon unloading so long as the reaction of the elastic skeleton is less than the stress applied upon loading, which is the case.

Apparently, one can only separate the reversible part of creep from the permanent part, which last can include the plastic creep, plus a part of the viscous creep. This separation is what was done by Freudenthal and Roll [83] and by Glucklich [99], proceeding by unloading at different ages as indicated in figure 34, determining for each age of unloading the irreversible deformation. Leaving out of consideration the creep and the possible evolution of the concrete during unloading, the curve obtained represents the irreversible part of creep that has been called secondary shrinkage by contrast with the primary creep or viscoelastic creep.

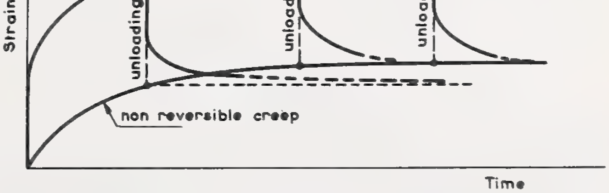

FIGURE 34. *Irreversible deformation after unloading at different ages.*

Is creep indefinite?

This question is highly important and not yet resolved. For this to be so, there must subsist a permanent viscous phase not included in the visco-elastic behavior associated with the elastic skeleton. This phase would then have as its law of deformation:

$$\frac{d\Delta_v}{dt}=a(t)$$

where $a(t)$ is a decreasing function with t. In order to know whether $a(t)$ approaches zero for t approaching infinity, one would have to know the evolution of creep over a period of tens of years.

What do we know about the law of creep with constant load, humidity, and temperature?

This law may be the combination of three phenomena:

—an elasto-plastic creep that is partially reversible:

$$\frac{d\Delta_p}{dt}=\dot{C}(t)(\Delta_{mp}-\Delta_p) \qquad \Delta_p=\Delta_{mp}e^{-C(t)}$$

—an irreversible viscous creep:

$$\frac{d\Delta_v}{dt}=\dot{A}(t) \qquad \Delta_v=A(t)$$

—a wholly reversible visco-elastic creep:

$$\frac{d\Delta_e}{dt}=\dot{B}(t)(\Delta_{me}-\Delta_e) \qquad \Delta_e=\Delta_{me}e^{-B(t)}.$$

The interaction of these phenomena which we qualify in rheology as laws of Newton and of Kelvin justifies the use of models in which one combines springs, dash-pots, friction, and return valves. This procedure leads to calculations that are extremely complicated and at the same time of great interest. Their practical use, however, remains uncertain [83, 99, 100].

If we simply superpose the three types of deformation, we find:

$$\Delta=A(t)+\Delta_{me}e^{-B(t)}+\Delta_{mp}e^{-C(t)}.$$

Now $B(t)$ must be a function similar to $A(t)$ to within one factor. The form of this function must be deducible from the unloading curve. Its form is viscous but depends on age, so that:

$$A(t)=\frac{\alpha t}{f(a)}$$

where $f(a)$ is an increasing variable of time, thus:

$$\Delta(t)=\left[\Delta_{me}e^{-\frac{\alpha t}{f(a)}}\right]+\left[\beta\frac{\alpha t}{f(a)}+\Delta_{mp}e^{-C(t,a)}\right].$$

The first term between brackets represents the continuous part of the creep and the second term the part limited to Δ_{mp}. This relationship is not very different from what McHenry proposes [75].

There is nothing, moreover, to prevent seeking an empiric variable

$$F(t) \text{ with } \Delta(t)=\beta\frac{\alpha t}{f(a)}+\Delta_m[1-e^{-F(t)}]$$

where the second term includes the viscous elasticity, the latter effect not being separated during loading. If, in addition, we consider that the first term is negligible compared to the second, we come back to the equation $\frac{d\Delta}{dt}=(\Delta_m-\Delta)F(t)$. For the moment, it does not seem possible to go much further in these calculations.

Is creep linked to shrinkage?

This question is both simple and complex. Without any doubt the concretes that have the greatest shrinkage have the most marked creep. But to say that creep is a shrinkage under load is in a sense a play on words. From the hygrometric point of view there is certainly a dependency between creep and shrinkage, while it is not certain that this relation is biunivocal; it is probably more correlative than functional. In other words, the two phenomena appear more precisely linked to a form of the hydrated phase that leads both to a similar evolution, that of a viscosity depending on time both for the one and for the other.

Concretes cured without a possibility of appreciable shrinkage nevertheless have a marked creep (adiabatic curing without exchange of water). This means, in any case, that there can be creep without shrinkage. A number of authors have considered this creep as a basic creep. But nothing, on the other hand, proves that creep in a dry atmosphere leads to a higher evaporation of the enclosed water as compared to a loaded test piece. The basic creep may be a factor of comparison that eliminates the dimensional parameter but does not appear to have any other effective value. We have seen, finally, that a concrete cured dry over a long period may, when placed in water, undergo a swelling without load and a supplementary shrinkage under load while the deformation remains the same, with or without load, over a period of drying that follows the placing in water (figs. 27 and 28). It is probable that placing in water leads either to an increase in the volume of the hydrated phase for a concrete cured dry or to a continuation of hydration, which endows the latter, through the lessening of its viscosity and its rigidity, with a new possibility of deformation. This hypothesis would likewise explain the increase in the elastic recovery for a test piece that is unloaded and placed in water (fig. 32). Let us not forget, however, that the creep of a concrete cured in water is less than for dry curing, and this appears contradictory. We must then suppose that curing in dry air does not permit a complete hydration and that it is the resumption of this hydration that gives rise to a new creep. This hypothesis does appear to be confirmed by the measurements of strength and of modulus of dynamic elasticity. We should then have to know whether a concrete hydrated permanently in water for a long period presents or does not present a resumption of creep after drying and fresh humidification. But we have no knowledge of any such experiment. T. C. Hansen [87] puts forth the hypothesis that creep is encouraged by any movement of dampness; alternate wetting and drying should give a higher and more rapid creep. This would mean that concrete is a thixotropic material.

Pickett [49] suggests that creep constitutes an accleration of shrinkage, which accordingly would have the effect of separating certain groups of particles and thus diminishing the rigidity. But this mechanism does not, apparently, explain the resumption of creep upon placing in water.

We see, finally, that the detailed explanation of the mechanism of creep on the scale of structure has not yet been given without possible challenge.

How does creep depend on humidity, on evaporation, and hydration?

Creep increases when evaporation occurs in dry air, that is to say when the evaporation is greater, no matter what may be the state of curing, hence of previous hydration. We have seen, however, that the creep deformation under load that is added to that of shrinkage without load does not lead to loss of weight, or therefore to a measurable supplementary loss of water. The explanation for this behavior is not easy to find. T. C. Hansen's surmise is very ingenious, but it does not explain the cessation of creep in a period of drying after wetting, if this fact remains confirmed by other experiments. But instead of saying, as does this author, that the diffusion of water favors movement, we might suppose that the chemical phenomenon of hydration by the molecular movement that it produces is a factor in softening of the binding phase. There may thus be a visco-plastic creep of which the speed is all the more limited, given equal hydration, as the hydrated phase is more considerable, and a viscous and visco-elastic creep of which the speed increases at the same time as the speed of hydration. We might describe this in a simplified and phenomenological way such as:

$$\frac{d\Delta}{dt}=\frac{A(t)}{H}+\frac{B(t)}{H}\frac{dH}{dt}$$

where H represents the volume of hydrated binder, the first term indicating the plastic creep and the second the viscous creep.

I hope I may be allowed an approximation suggested solely by the drafting of this report and which so far has benefited by no direct verification. Such a hypothesis, however, makes it possible to interpret several apparently contradictory phenomena such as:

—the more rapid stabilization of creep in a damp medium for a lesser final value,

—the increase of visco-elastic recovery by placing in water,

—the resumption of creep by humidification and its stoppage by drying.

The maturing of a concrete represents, in a sense, its degree of hydration, whether it be represented in volume, in mechanical strength, in rigidity, etc. It is dependent upon time, temperature, the medium in general. In fact it is homologous to the variable H indicated above. An excellent interpretation of it is to be found in a recent report by Ross [101] and we believe that herein may be found matter for broad interpretations.

We said earlier that creep may increase indefinitely so long as a viscous phase subsists, and we wrote $\frac{d\Delta_v}{dt}=a(t)$. We can compare this point of view with what has just been set forth and write: $a(t)=\frac{b(t)}{H}\frac{dH}{dt}$. Viscous creep of the Newton type disappears only when hydration is completed. It disappears more rapidly in curing in water than in dry air where the hydration is considerably slowed down; in the latter case, it resumes upon placing in water.

In the case of curing in constant atmosphere and taking $\beta(t)=\beta$ as a constant, we find that the final viscous deformation is:

$$\Delta_{mv}=\beta\log\frac{H_m}{H_0}$$

where $\frac{H_0}{H_m}$ represents the relative hydration at the moment of loading compared to the total hydration. If we assume that the relative hydration is proportional to θ, or $H_0=H_{m0}\theta$ where H_{m0} is the degree of hydration at time $t=0$ of the piece cured in water, we find:

$$\Delta_{mv}=\beta\left[\log\frac{H_m}{H_{m0}}+\log\frac{1}{\theta}\right]$$

The first term between brackets represents the effect of viscosity for curing in water, the second represents the additional deformation for curing in air in an atmosphere of relative humidity θ. Now $\frac{\log 1/\theta}{1-\theta}$ varies between 1 and 1.20 for θ included between 0.99 and 0.6. This means that the viscous creep must be approximately proportional to $(1-\theta)$; which is not in contradiction with the experiments.

This calculation has been made without any other pretension than to show the comparability of its principle with the results already known and to propose to investigators a line of reasoning.

How does creep depend on volume?

The influence of the absolute volume on creep is undeniable; it is generally explained by the rapidity of evaporation. Concrete cured in water has less creep than that cured in a closed medium, and creep in a closed medium is less than in a dry atmosphere.

Two explanations are then possible, if not complementary. The first involves the internal stresses [102, 79]. Creep and shrinkage begin on the surface and lead to a concentration of stresses toward the core. The latter then undergoes a creep in a moist medium less pronounced than the surface creep. If the effects were simply compensated there would result a delay in the deformation, but as the compensation does not occur for bulky pieces, there results likewise a lessening in the final creep. The second explanation derives from the interpretation of what we have just said in connection with hydration. The bulkier a piece is, the slower its mean evaporation is, and the closer, at the beginning, it comes to curing in a closed space. When desiccation reaches the core, the hydration is far advanced, H is large and $\frac{dH}{dt}$ is slight. We know that a preliminary curing in moist air diminishes the final creep in dry air. Here this process is progressive but leads to similar effects. Finally, the bulky pieces creep less because they are better hydrated. The pieces protected from evaporation by surface humidification or by a protective device maintained for a sufficiently long time must have a lower and more rapidly stabilized final plastic deformation.

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Discussion

E. Torroja and C. de la Peña

Introduction

The shrinkage and creep of the gel constituted by cement and water are better studied when:

(a) No gravel and coarse sand are present, because the stones restrain very much the free deformations of the paste and put it in tension, and

(b) The specimen has a thin section, because the differences in humidity and temperature between its core and surface give rise to internal stresses.

In the testing procedure described here, we use mortar specimens having the form of a tube with a very thin wall.

The surface per unit of volume of these pipes is 10 cm^2/cm^3, which amounts to 9 times that of the 4 x 4 x 16-cm prisms and 30 times that of cylinders 15 cm in diameter and 30 cm in length.

Using pipes of such a high specific surface speeds up the process of exchanging water between the specimen and the surrounding air, and so it is possible to reach the final equilibrium in a short time.

The results of the first tests carried out with these pipes were submitted to the RILEM Colloquium upon Shrinkage and Creep of Mortars and Concretes held in Munich. The paper was published in Bulletin No. 3 of RILEM (July, 1959).

Just a few more results are now available, but we think the procedure may be of interest to the attendants at the Symposium, because it seems a proper method for studying among other things the relationships between the composition, fineness, etc., of cements and their shrinkage and creep.

Specimens

Form and Dimensions

The specimens are pipes with the dimensions given in figure 1. The walls of the tubes are a little thicker at their ends in order to prevent the anomalous failures observed when these pipes are made of constant wall thickness throughout their length and tested in compression.

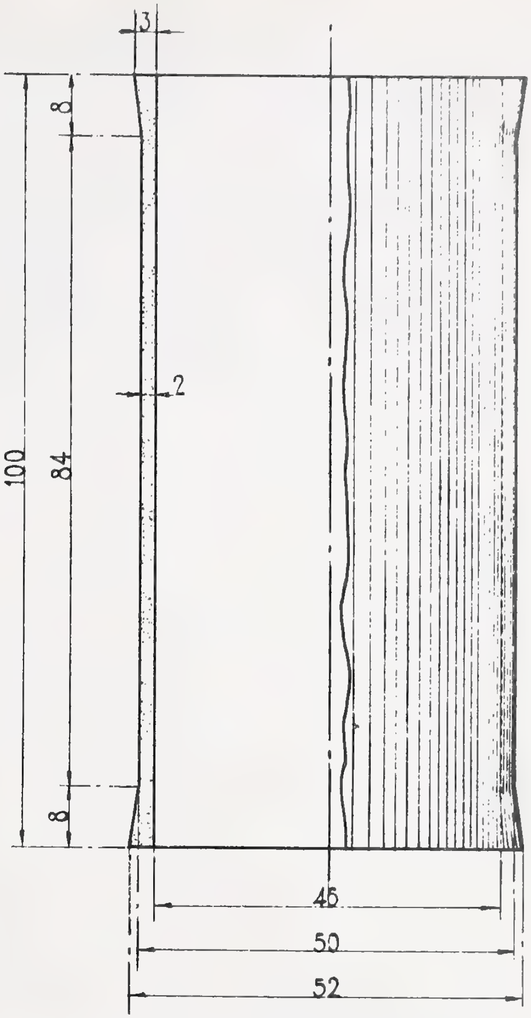


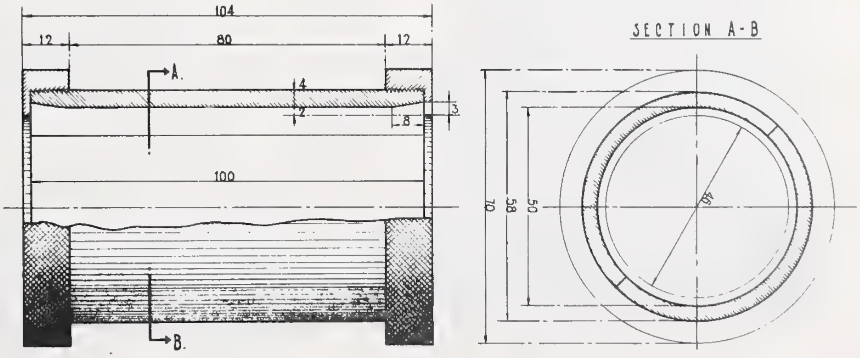
FIGURE 1. *Dimensions of pipe specimen.*
(Dimensions in mm.)

Molds

Figure 2 shows the mold employed. All the molds are made of stainless steel in order to prevent any corrosion, which would be more harmful in this case than in others because of the thinness of the specimen wall.

The side wall of the molds is a tube divided in two halves lengthwise. These two halves are

FIGURE 2. *Specimen mold.*
(Dimensions in mm.)



held together by two like pieces, one on each end of the tube. Both pieces have a 46-mm central circular hole which provides, with the 50-mm inside diameter of the steel tube, a 2-mm mortar wall.[1]

Mortar

In the tests referred to in this paper we have used a common portland cement and a very pure siliceous sand in which the particles ranged from 0.15 mm to 0.30 mm in diameter. The proportions by weight of the mortar were 1:1.

The mixing water was adjusted in order to obtain a flow of 40 ± 5 percent on the RILEM flow table for mortars. This flow corresponds to a workable plastic consistency.

The resulting water/cement ratio was 0.34.

Molding

The essentials of the procedure are the following:

The mold is held by the left hand, with the palm upwards and the axis of the mold practically horizontal. With a tool that is a sort of a sharpened straight rule, a small amount of mortar is put in on the lower part of the mold, evenly distributed throughout the length of the steel tube, gently pressed and tapped with the tool and made level with its sharpened edge, which is moved meanwhile as it bears upon the edges of both holes of the mold. The mold is then turned through a small angle around its axis with the left hand, and another portion of mortar is placed inside in the same way. The filling goes on until the whole interior surface of the steel tube is properly covered by a 2-mm layer of mortar (fig. 3).

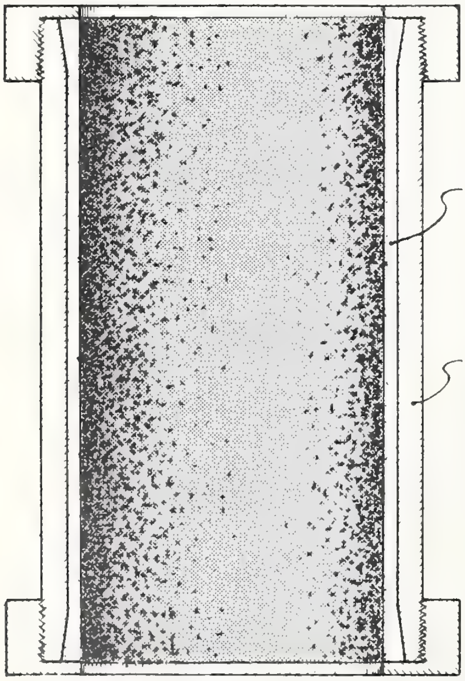


FIGURE 3. *Longitudinal section of specimen in mold.*

With mixes neither too dry nor too wet, such as that of mean consistency, which we have used, the procedure described works well, though some training of the laborer is necessary anyway.

The molding is performed in a room at 20 ± 2 °C and 98 ± 2 percent rh.

Curing

The mortar pipes are left in their molds for 24 hr in the same room where they are molded. Then the molds are removed, and the specimens are immersed in water at 20 ± 1 °C until just the moment of their test.

Apparatus

All apparatus is in a room whose temperature is 20 ± 1 °C.

Device for Measuring Shrinkage

The apparatus to measure the shrinkage of the pipes is shown in figure 4. It has a central airtight chamber which includes the specimen under test and a hollowed ring container at the bottom for the moisture-conditioning water-glycerine solution.[2] The top of the chamber is a thin sheet of rubber to allow the stainless steel block that rests on the upper end of the pipe to descend as the pipe shrinks.

A dial gage is rigidly attached to the beam at the upper part of the apparatus. The tip of its stem, which is in contact with the center of the block, follows the shortening of specimen.

In order to make possible the changing of the water-glycerine solution during the tests, the container has a hole in its lower part through which, when it is necessary, the already altered solution can be extracted; meanwhile another open hole in the glass tube lets air in and so prevents any vacuum in the chamber.

Once the container is empty, a fresh solution is injected through the same hole, with the vent valve open as before, to prevent any unwanted pressure in the specimen chamber.

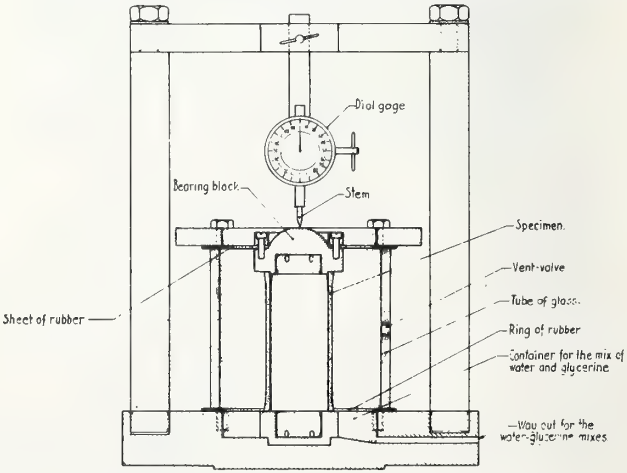


FIGURE 4. *Apparatus for measuring shrinkage.*

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[1] The mortar pipe wall thickness equals half the difference of the two before-mentioned diameters, as will be seen in a following paragraph.

[2] The solutions of water and glycerine are prepared and checked in accordance with the ASTM Recommended Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions (E 104–51).

Device for Measuring Creep

The apparatus used to measure the creep is essentially the shrinkage device mounted in a framework which has a rubber cylindrical pneumatic chamber at the bottom and a big steel beam at the top to compress between them the specimen under test.

As can be seen in figure 5, the dial-gage stem is not now in contact with the bearing block as before, but with the big beam of the charging framework. Therefore, it is in this case the body of the gage that moves, going up as the specimen shortens with time under the load applied.

Before the tests were started, a graph was drawn plotting the kg/cm² of air pressure in the pneumatic chamber against the kg of compression between the bearing blocks.

To carry out the third group of tests described below, the creep devices were somewhat modified. No water-glycerine mix was used in these tests, and the whole chamber with the specimen was filled with water whose temperature was raised to and maintained at the specified figure. For this purpose, an electric resistance, a thermoregulator, and a thermometer were put inside the chamber of each apparatus. The variations registered about the desired temperature were never greater than ± 1 °C.

Tests

Three groups of tests were carried out in order to see the following things:

(1) The reproducibility of the results of shrinkage and creep measurements,

(2) The relation between load and creep, and

(3) The influence of temperature upon creep.

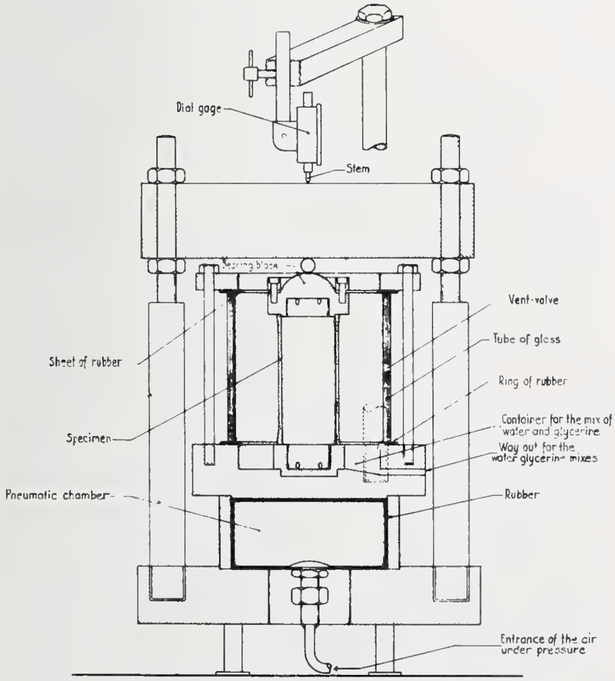
Dial gage
Stem
Bearing block
Vent-valve
Tube of glass
Sheet of rubber
Ring of rubber
Specimen
Container for the mix of water and glycerine
Way out for the water glycerine mixes
Pneumatic chamber
Rubber
Entrance of the air under pressure

Figure 5. *Apparatus for tests of creep.*

Reproducibility of Results

Shrinkage. After a curing time of 28 days in water at 20 ± 1 °C, 15 pipes made with the mortar and in the conditions described above were put for 21 days in the shrinkage devices with the proper water-glycerine mix to maintain a relative humidity of 50 percent in the specimen chamber. The room with the apparatus was kept at 20 ± 1 °C.

The shrinkages were measured every 24 hr, and it was observed that the major part of the shrinkage of the pipes takes place in the first week, as can be seen in figure 6, where the curve of the mean values has been drawn, as well as the curves joining the points of minimum and maximum shrinkage.

The shrinkage of each pipe appears in table 1, as well as the mean values, the standard devia-

Table 1. *Shrinkage of pipe specimens at ages up to 28 days*

Pipe No.	Shrinkage in °/₀₀		
	At 1 day	At 7 days	At 28 days
1	0.81	1.19	1.28
2	.78	1.16	1.28
3	.82	1.16	1.31
4	.58	1.08	1.16
5	.68	1.07	1.14
6	.81	1.19	1.23
7	.80	1.21	1.31
8	.81	1.14	1.18
9	.79	1.19	1.30
10	.82	1.21	1.27
11	.80	1.17	1.25
12	.75	1.15	1.25
13	.71	1.13	1.23
14	.70	1.15	1.18
15	.74	1.18	1.16
Mean value	.75	1.16	1.24
Standard deviation	.066	.040	.052
Coefficient of variation, %	8.80	3.44	4.19

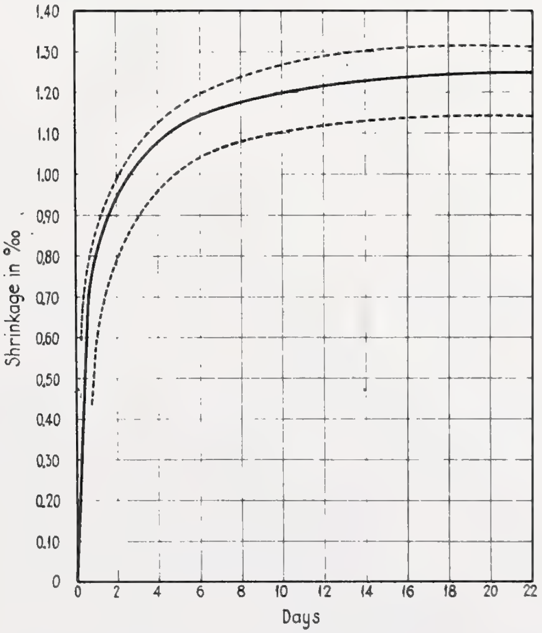

Figure 6. *Shrinkage of specimens in relation to period of storage at 50 percent rh.*

tions, and the coefficients of variation (relative deviations).

The results show that:

(a) The final value of shrinkage is reached very quickly, and

(b) The different final values obtained are rather alike.

Creep. Once the final value of shrinkage was practically reached, the 15 pipes were removed from the shrinkage apparatus, put in the creep devices, where the temperature and relative humidity were the same as before (20 °C and 50 percent rh), and loaded at 50 percent of their compressive strength.

The shortenings were measured every 24 hr. In figure 7 appear the curve of the mean values as well as the curves joining the points of minimum and maximum shortening.

The creep of each pipe can be seen in table 2, as well as the mean values, the standard deviations, and the coefficients of variation. The results obtained show that the relative differences are of the same order as in other tests of cements.

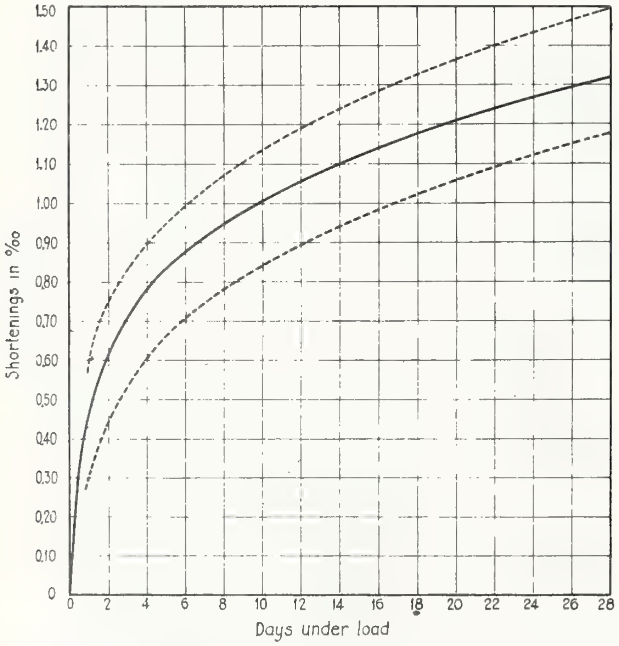

Figure 7. *Creep of specimens in relation to period under load.*

Loads and Creep

Twelve pipes made and cured as before (28 days in water at 20 °C) were allowed to shrink for 21 days in air (20 °C temperature and 50 percent rh) and then put for 28 days in the creep devices. Three specimens were under each of the following loads: 20, 30, 40, and 50 percent of their compressive strength. The temperature and relative humidity of the air surrounding the specimens while being tested for creep were as before (20 °C and 50 percent rh).

Table 2. *Creep of pipe specimens at ages up to 28 days*

Pipe No.	Creep in ‰					
	At 1 day	At 3 days	At 7 days	At 14 days	At 21 days	At 28 days
1	0.47	0.70	0.91	1.12	1.25	1.35
2	.46	.66	.80	.93	1.05−	1.18−
3	.58	.83	1.02	1.23+	1.36	1.48
4	.53	.77	.99	1.21	1.37+	1.50+
5	.59+	.83+	1.03+	1.13	1.26	1.35
6	.52	.74	1.00	1.15	1.29	1.39
7	.49	.68	.89	1.04	1.14	1.25
8	.45	.70	.92	1.12	1.26	1.33
9	.47	.70	.92	1.14	1.25	1.34
10	.39	.68	.89	1.05	1.16	1.25
11	.44	.69	.89	1.11	1.23	1.34
12	.32−	.53−	.74−	.94−	1.11	1.28
13	.42	.64	.83	.99	1.09	1.19
14	.55	.81	1.00	1.21	1.32	1.39
15	.47	.69	.85	1.07	1.16	1.25
Mean value	.48	.71	.91	1.10	1.22	1.32
Standard deviation	.069	.075	.082	.089	.094	.090
Coefficient of variation, %	14.37	10.56	9.03	8.09	7.70	6.81

Figure 8, drawn with the mean values of the shortening at 1, 2, 3, and 4 weeks, shows that the creep is practically proportional to the load applied when this is not greater than 50 percent of the compressive strength of the pipes.[3]

Temperature and Creep

Thirty pipes cured as in the two previous groups of tests (28 days in water at 20 °C) were put in the creep devices and tested under water for 7 days, as follows:

Number of pipes	Temperature of the water	Load applied (percentage of the compressive strength)
	°C	%
5	20	20
5	20	40
5	35	20
5	35	40
5	50	20
5	50	40

With the mean values of the results obtained after 7 days of testing we have drawn figures 9 and 10 where it can be seen that:

(a) Regardless of temperature, the deformation of the pipes after 7 days of testing is proportional to the load applied up to 40 percent of their compressive strength, and (b) Creep under water is also proportional to temperature in the range from 20 to 50 °C, after 7 days under load.

Final Considerations

We realize that the limits of our conclusions are very narrow, because of both the small number of tests and the very short time under load of the pipes.

For instance, the effect of temperature may be quite different if the specimens are tested in dry hot air instead of under hot water.

On the other hand, it is very probable that the influence of temperature upon creep becomes less

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[3] This conclusion seems to be in contradiction with the statement that appears in our previous paper; but it is necessary to take into account the differences in the procedures followed then and now in testing the pipes as well as in the form of presenting the results.

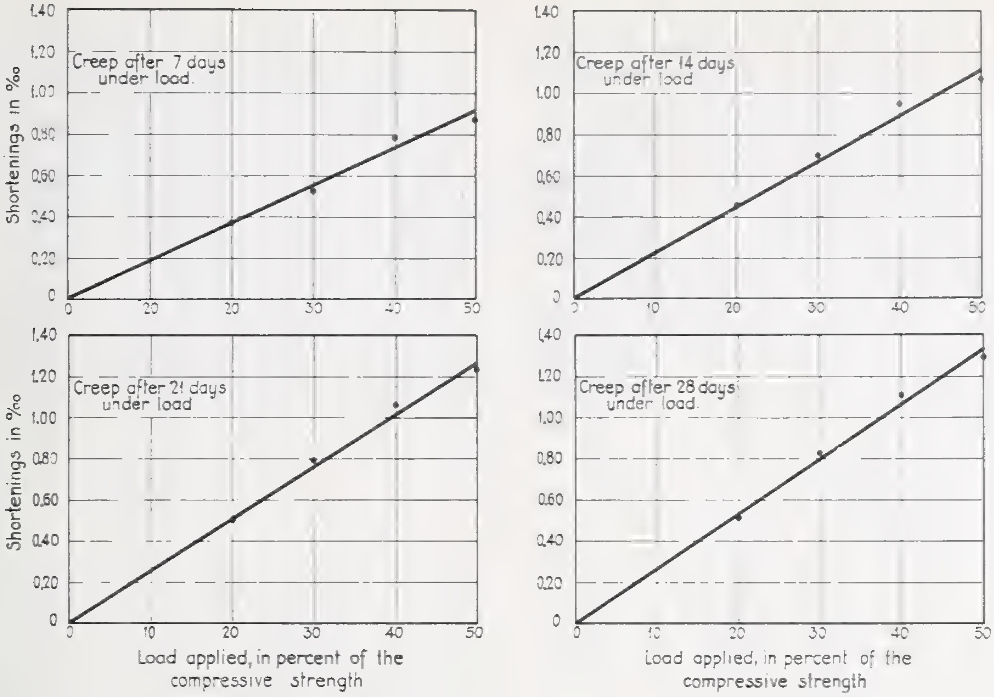

Figure 8. *Creep as function of load for various periods under load.*

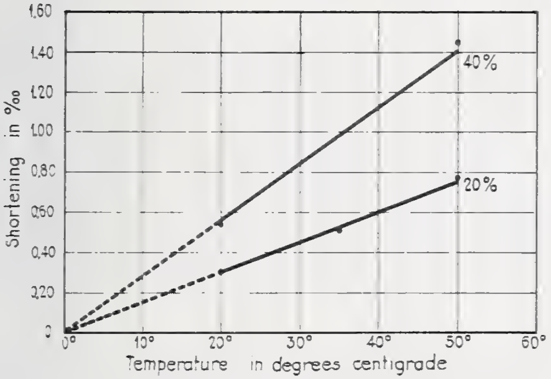

Figure 9. *Creep under water with two different loads, in percent of the compressive strength.*

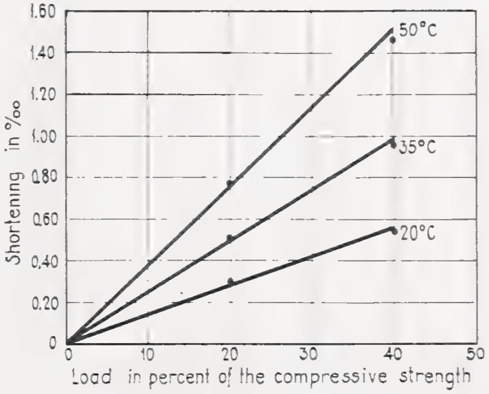

Figure 10. *Creep under water at three different temperatures.*

and less important as the time under load increases.

Therefore, much further research is necessary before coming to firm conclusions upon the matters dealt with in this paper; especially, as far as the effect of temperature upon creep is concerned.

We hope that this paper will give to the members of the Symposium a guess about the possibilities of the testing procedure employed in carrying out studies of the shrinkage and creep of cements, not only without the microcracking caused by gradients of humidity and temperature between core and surface, but also without the uncertainty about the real humidity and true temperature of the different parts of the commonly used thick specimens. In order to obtain reliable results, the conditions of humidity and temperature of not only the surrounding air, but, above all, of the specimen under test, need to be well defined.

Discussion

R. R. Hattiangadi and P. J. Jagus

The swelling of cement under hydration is a chemical phenomenon accompanying hardening. It has been observed that swelling continues for a longer time and is also of greater magnitude in those cements which harden or hydrate slowly than in rapid-hardening cements. It would be of interest to know whether or not the internal buildup of strength plays a part in resisting the apparent increase of volume through swelling.

The observation regarding the boiling water test for cement, popularly known as the Le Chatelier test, being advocated for the rapid determination of chemical unsoundness of cement is of significance. It is mentioned that the test brings out very rapidly the presence of unhydrated

CaO and MgO if the boiling is continued for 5 hr. Contrasted to this, the British Standard Specification B.S. 12, which has adopted this test, specifies the boiling period of the specimen at 1 hr. In our Indian Standard Specification for ordinary and rapid-hardening cements, this boiling time was originally prescribed at 30 min but on later consideration it was increased to 3 hr in the subsequent revisions of the standard. If a longer period of boiling is observed to bring about reliable results with greater rapidity, it is worth considering whether standard specifications which stipulate the Le Chatelier test for determining the soundness of cement should revise upwards the period of boiling on the basis of any standardization work that may have been done in this direction.

It would also be worthwhile to look comparatively at the two parallel tests for soundness of cement, namely, the Le Chatelier test and the autoclave expansion test. Whereas autoclaving the specimen at a high temperature and a pressure of 310 psi for 3 hr can bring about a rapid hydration of the CaO and MgO, one wonders whether the full physical effects of this hydration in terms of the accompanying volume change will be brought about in the specimen, since it is simultaneously being subjected to such a high pressure. The Le Chatelier test, on the other hand, permits an almost unrestricted swelling of the specimen. This test, which is easier to adopt, is generally prescribed more frequently than the autoclave test, and if any further advantage in reliance and rapidity of the test could be secured by increasing the period of boiling, such a change would be worthy of adoption in the specifications.

The paper brings out important aspects of the physical properties of concrete in respect to the volume changes under varying conditions. Cements which have been matured under water show lower coefficients of thermal expansion than those cured under lower relative humidities of 50 and 75 percent.

The observation is made that cement paste protected against evaporation by an impermeable membrane shrinks due to the internal desiccation of the mass by hydration of cement consuming the internal humidity. This phenomenon has a practical significance in respect to concretes which are cured with the help of solid and liquid membranes. In the absence of replacement of that part of the free water which is chemically taken up for hydration, the mass will tend to shrink, developing distress in the body of the concrete at an early age when it has very little strength to resist the stress.

The work of Meyers, Verbeck, and others has shown that carbonation of a concrete specimen diminishes the reversible shrinkage and gives it greater stability against volume variations due to changes in relative humidity. It may be of interest to note that this fact is now being usefully exploited by several American manufacturers of concrete products and masonry block. It has also been found in practice that the strength of carbonated concrete increases with the amount of carbon dioxide absorbed and the amount absorbed increases in turn with the amount of water present. The industrial application of this idea is made possible at very little extra cost with the help of waste flue gases which are diverted into the curing chamber. This treatment is also known to help in reducing the permeability and efflorescence of the concrete.

The author, in the latter part of his paper, has dealt with load-deformation characteristics of cement and concrete. I am sure that exhaustive information compiled on elastic, and plastic, creep behavior of concrete will be of immense value to the men in research as well as in construction.

Discussion

Myron A. Swayze

In his paper on "Volume Changes in Concrete", Robert L'Hermite is concerned with all phases of change in volume; not only in concrete, but in mortars and cement pastes as well. This discussion is limited to the consideration of the shrinkage due solely to drying of these three types of specimens in air of 50 percent rh for various types of portland cement.

It has long been considered that increasing the fineness of cements leads to higher drying shrinkages in pastes, mortars, and concretes. It has also been assumed that when differences in the shrinkage characteristics of a group of cements are found in neat pastes or rich mortar specimens, proportionate differences will be found in the shrinkage of concretes made with these products. It is the purpose of this discussion to show that neither of these assumptions is tenable, so far as the behavior of portland cements in normal concrete is concerned.

The Lone Star Cement Research Laboratory at Hudson, New York, has been conducting volume-change tests on 3 x 3 x 10-in concrete specimens for many years, using mixtures of cement and nonreactive siliceous sand and gravel aggregates ranging from 329 to 846 lb of cement per cubic yard (195 to 500 kg/m^3) with water sufficient to produce slumps of 2 and 6 in. Up to this year we have not made similar tests on mortar or neat-cement specimens, due to the tendency of some otherwise well-informed engineers to translate the higher shrinkages exhibited by such specimens into terms of contraction in inches per 100 feet of concrete pavement, and to draw erroneous conclusions from these figures.

This year two proposals to limit volume changes of portland cements by specification were proposed in the United States. One test consisted of molding a normal consistency neat paste in 1 x 1 x 10-in molds moist curing for 24 hr., measuring, and then storing in air of 50 percent rh for 48 hr. A limit of 0.10 percent shrinkage at the age of 72 hr. was suggested. The second proposal was to use a 1:2 graded Ottawa sand mortar, cured in 1 x 1 x

10-in molds for 24 hr, then measured and immersed in water for 48 hr. Expansions were then measured, after which specimens were placed in 50 percent rh air storage for an additional 4 days. The proposed limits were 0.01 percent on 48 hr expansion in water and 0.04 percent on subsequent shrinkage after 4 days of drying. Both types of test would reject a majority of cements tested under their conditions and limits.

To check the volume changes obtained by these methods against similar data on concrete specimens, cement samples of all ASTM Types, except IV and V, were used for production of neat and 1:2 mortar bars. These samples had been preserved in sealed metal cans and represented cements in a comprehensive series of concrete tests, started in 1957 and now nearing completion, on some 56 cements of different types. The 42 cements included in this discussion are those on which we have information through the age of 1 yr.

Our figures on concrete shrinkages are based on averages of 18 concrete specimens for each cement. These 3 x 3 x 10-in specimens represented three rounds of batches mixed on successive days with cement contents of 423, 564 and 705 lb of cement per cubic yard (250, 334, and 417 kg/m^3) with 2- and 6-in slumps. Past experience has shown that the 1-yr tests on such specimens are at or very close to their ultimate shrinkage. Design of all concrete mixes was based on a total fineness modulus of 4.85 (including the cement volume as 0.00 FM) for normal concretes, and 5.00 for air-entraining varieties. Aggregate grading was from 0 to 1½ in, all of siliceous sand and gravel. Gravel larger than 1¼ in was discarded in molding volume change specimens. Curing of all concrete specimens was in molds for 24 hr, 2 days in fog at 23 °C, followed by continuous storage in air of 50 percent rh.

Data on neat pastes and 1:2 mortars are on averages of three specimens for each cement. Curing of neat bars was 24 hr in molds, followed by immediate storage in air at 50 percent rh after removal from molds and initial measurements. The mortar bars were cured 24 hr in molds, 48 hr in water and then in air at 50 percent rh until 28 days after molding. Finally, all neat paste and mortar bars were subjected to 48-hr drying at 105 °C, then returned to 50 percent rh storage for 24 hr before final measurements at 31 days.

The following table shows average percentages of linear dimensional change for each type of cement in the three types of test. In all cases shrinkages are related to the initial measurements after removal from molds, rather than to those made after the 48 hr of fog or water curing. The ages relate to ages of specimens after casting. Details on individual cements in each type classification are too lengthy to be discussed here, but will be published in the ASTM Bulletin early in 1961, following presentation of the data before ASTM Committee C–1 on Cement in December, 1960.

TABLE 1. *Dimensional changes of concretes, neat pastes, and 1:2 mortars after indicated time of storage at 50 percent* rh

Concrete Tests

Type of cement	No. of cements	w/C	% shrinkage after 1 day in molds, 2 days in fog				
			3 day	7 day	28 day	3 mo	1 yr
		%					
I	10	54.6	+0.001	0.012	0.035	0.048	0.060
IA	7	49.6	+.001	.012	.036	.050	.062
II	8	53.6	+.001	.009	.032	.047	.060
IIA	3	48.3	+.001	.009	.033	.046	.062
III	12	54.4	+.001	.011	.033	.047	.061
IIIA	2	51.1	+.001	.011	.035	.048	.062

Neat Pastes

			% shrinkage after 1 day in molds				
			2 day	3 day	7 day	28 day	Dried
I		24.6	0.061	0.092	0.152	0.221	0.428
IA		24.3	.077	.112	.180	.255	.459
II		24.6	.058	.090	.152	.211	.414
IIA		23.5	.062	.095	.159	.221	.425
III		26.5	.078	.122	.172	.243	.525
IIIA		26.0	.088	.125	.184	.255	.542

1:2 Mortars

			% shrinkage after 1 day in molds, 2 days in water			
			3 day	7 day	28 day	Dried
I		38.5	+0.002	0.055	0.096	0.139
IA		38.1	+.002	.058	.102	.152
II		38.3	+.002	.040	.075	.116
IIA		37.1	+.002	.046	.087	.131
III		38.7	+.005	.050	.089	.140
IIIA		38.0	+.002	.053	.093	.144

Considering these data, it becomes immediately apparent that the effect of type of cement on ultimate shrinkage of concrete is insignificant. The very finely ground Type III and IIIA products display no more shrinkage than normal-fineness cements, if differences of one or two thousandths of a percent can be neglected. On the other hand, specimens made with neat pastes would lead one to believe that Type II cements should display some 5 percent less shrinkage than Type I products, and 22 percent less than Type III cements, if we consider the data on dried specimens after 28 days of 50 percent rh storage as a measure of the ultimate shrinkage of neat pastes.

In a somewhat similar comparison in mortars, Type II cements again appear to have an advantage over Type I products in developing lower ultimate shrinkages. On the other hand, the high-fineness Type III cements display no significantly greater shrinkages than Type I cements, either at the age of 28 days or after drying.

The moral to be derived from these data is obvious. If we are interested primarily in reducing drying shrinkage due to cement in structures, we should always use the cement in concrete mixes—never in mortars or neat pastes that are subject to drying. Second, although molding and testing of concrete specimens with their larger bulk is more expensive and time-consuming, we should confine our testing to this medium if we are to avoid the arrival at erroneous conclusions from data derived from tests on neat pastes or rich mortars.

Discussion

T. C. Powers

Prof. L'Hermite is to be thanked for his prodigious task of assembling facts and ideas pertaining to volume changes of concrete. The scope of his discussion contributes toward a unified understanding of the various phenomena embraced by the subject.

Prof. L'Hermite refers to the observation that concrete shrinks or swells when its water content is decreased or increased, and says, "There is thus a relation between the movement of water and shrinkage that does indeed appear to be a 'cause-and-effect' relationship." At this point the wording suggests some reservation regarding the actual relation of cause and effect, but in other parts of the paper the widely held belief that water removal per se is the cause of shrinkage is adopted. For example, it is said that shrinking or swelling cannot occur when a specimen is kept in the saturated state. In another connection, it is indicated, correctly, that a sealed specimen may shrink because some of the water in it is effectively removed by chemical reaction—"self-desiccation"—but it is indicated that a sealed specimen cannot shrink in the absence of self-desiccation. In connection with the relation between shrinkage and creep, it seems to be suggested that since loaded and unloaded specimens lose the same amounts of water under the same conditions of drying, the extra time-dependent deformation of the loaded specimen cannot be ascribed to extra shrinkage caused by the load.

It is indubitably a fact that if the water content of cement gel changes, the volume of the gel will change too, but it is incorrect to say that if the water content of the gel does not change, the specimen cannot shrink or swell. This was proved from experiments carried out in this laboratory by R. A. Helmuth. He found that when a saturated specimen of cement paste was cooled at a steady rate, its *initial* rate of contraction was about 3 times as great as the normal rate of thermal contraction—29 millionths per degree as compared with 11 millionths per degree. The difference, 18 millionths per degree, represented shrinkage of the gel occurring while its water content was constant. Such shrinkage is caused by the appearance of tension in the water, related directly to the decrease of temperature. In a saturated specimen, the effect is transient because the tension induced by the drop of temperature becomes released by transfer of water from the capillary spaces (eventually from water outside the specimen) to the gel.

When Helmuth cooled a sealed specimen in which the water content was below the saturation point, the specimen contracted about 25 millionths per degree, of which about 14 millionths per degree was due to shrinkage, as discussed above. In this case, nearly all the evaporable water was in the gel pores to begin with, and thus there was not enough capillary water to relieve the increase in tension caused by the drop of temperature. The shrinkage caused by cooling in this case was therefore not transient, as it was for a saturated specimen.

In recent studies of old data I found that for all relative humidities above 50 percent the final amount of shrinkage of a laboratory specimen of mature paste (no unhydrated cement) is the product of internal hydrostatic tension and the mechanical compressibility of the specimen. The amount of shrinkage is nearly the same as would be produced by an externally applied, sustained, hydraulic pressure of the same intensity as the internal tension. The intensity of internal tension, that is the tensile stress, is given with adequate accuracy by Kelvin's equation. For example, at a humidity of 50 percent, the amount of shrinkage is the same as that which would be caused by an external hydraulic pressure of about 900 atm applied at the specimen boundaries. When the internal tension becomes canceled, as by saturating the specimen, the specimen expands *elastically* the same amount that it would from the removal of an equal external pressure. (The first shrinkage is greater than the first swelling because of irreversible changes in gel structure that are produced by the first loading of the structure by the internal tension.)

Such results are to be expected from the theory that Prof. L'Hermite ascribes to Freyssinet, called the Capillary Theory. As commonly given, this theory ascribes the state of water tension to the presence of curved water surfaces—meniscuses. However, it now appears that meniscuses should be regarded as the *result* of water tension, rather than the cause, and when this concept is adopted, the capillary theory and its apparent rival are in harmony under the limited range of conditions within which the capillary theory is applicable.

Since shrinkage is mechanical, partly elastic compression, a cylindrical specimen subjected to an axial load and to drying simultaneously is being subjected to a uniaxial pressure and a triaxial pressure simultaneously. Each pressure is capable of producing elastic, time-dependent, and irreversible deformations. This should be taken into account in attempting to discover the relationship between shrinkage and creep.

Shrinking, swelling, creep, and all such words do not correspond to intrinsic properties of a material. They are terms we have adopted to designate certain modes of behavior, usually of laboratory specimens, under changing internal and external forces. I believe we are now in a position to establish a unified picture of such behaviors in terms of known forces and corresponding displacements.

Paper V–S1. Creep of Aluminous Cement Concrete*

A. M. Neville and H. W. Kenington

Synopsis

Data on creep of aluminous-cement concrete are presented, and it is shown that the order of magnitude of creep is the same as that of portland-cement concrete, when compared on the basis of the stress-strength ratio. Ambient humidity is also shown to have a similar effect on both types of cement.

These similarities, and the influence of the strength of concrete on creep, are thought to suggest that the gel-space ratio of the hydrated paste is the primary factor in creep.

Résumé

Des données sur le fluage du béton de ciment alumineux sont présentées, et il est indiqué que l'ordre de magnitude du fluage est le même que celui du béton de ciment Portland, quand on les compare sur la base du rapport contrainte-résistance. Il est prouvé également que l'humidité ambiante a un effet semblable sur l'un comme sur l'autre ciment.

Ces similitudes, et l'influence de la résistance du béton sur le fluage semblent pouvoir suggérer que le rapport gel-espace de la pâte hydratée est le facteur principal dans le fluage.

Zusammenfassung

Werte für das Kriechen des Tonerdezementbetons werden angegeben, und es ist angedeutet, daß die Größenordnung des Kriechens dieselbe wie für Portlandzementbeton ist, wenn der Vergleich auf der Basis des Verhältnisses Spannung/Festigkeit gezogen wird. Die Umgebungsfeuchtigkeit hat einen ähnlichen Einfluß auf beide Zementarten.

Diese Ähnlichkeiten und auch der Einfluß der Betonfestigkeit auf das Kriechen werden so gedeutet, daß das Verhältnis Gel/Volumen der hydratisierten Paste den größten Einfluß auf das Kriechen ausübt.

Introduction

Recent advances in the study of creep of concrete have brought us closer to a full understanding of the nature of creep and thus to a better appreciation of the physical and chemical factors in the behavior of hydrated cement paste. A study of creep [1] [1] and of creep recovery [2] of sand-cement mortars made with cements of different compound compositions, has been reported earlier; in this paper the results of creep tests on aluminous-cement concrete are presented. In addition to widening the field of study of the influence of the type of cement, the data presented here give some indication of the creep behavior of aluminous-cement concrete—a material used structurally under conditions in which creep may be of great importance.

Comparatively little is known about the creep properties of this cement; Glanville [3] reported his pioneer tests in 1930, and their long-term extension was described in 1939 by Glanville and Thomas [4]. Only one mix was used in those tests, and, of course, at the time the various factors in creep were not realized. This remark must not be construed as a criticism of Glanville's work, as, indeed, it was he in England and Davis in the United States who brought to our notice the entire problem of creep and its wide implications.

One important feature of Glanville's tests is that he found the creep of aluminous-cement concrete when stored dry to be less than when stored wet; this behavior would appear to be contrary to that exhibited by all portland cements, and probably for this reason it has been quoted again and again during the last 30 yr. A probable explanation of this anomaly will be given in this paper.

Test Details

Cylindrical concrete specimens were subjected to a sustained load in a simple lever-frame apparatus, operating on the principle of a nutcracker. This apparatus as well as the storage cabinets and the method of loading and the various details of procedure have all been described in a previous paper [5]. The specimens were stored at 20±0.1 °C, and for the main series of tests at a relative humidity of 95 percent.

The cement used was of English manufacture; its properties are listed in table 1, and it can be

TABLE 1. *Properties of cement*

Setting time (Vicat): initial, 4 hr 15 min; final, 4 hr 35 min
Specific surface (Lea and Nurse): 2910 cm²/gm

Oxide composition								
Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	FeO	TiO_2	MgO	Loss on ignition
Percent	4.87	38.35	38.35	9.43	6.00	1.99	0.74	0.16

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Manchester, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

seen that it is a fairly typical aluminous cement, although perhaps with a rather low alumina-lime ratio.

The aggregate was of siliceous origin; well rounded gravel for the 3/16 to 3/8-in. fraction, and crushed gravel for the sand fraction. The grading curve is given in figure 1.

Table 2 lists the mix proportions of the various mixes used, and also the values of compressive strength of 3-in. test cubes and of cylinders. It should be noted that the cylinders, which were of the same dimensions as those used in the actual creep tests, were not of standard proportions, but were 9¼ in. long and 2 in. in diameter. These dimensions were governed by the limitations of the creep apparatus [5]. Since, however, the strength data are mainly of comparative value, the high height-diameter ratio used is not thought to be of importance.

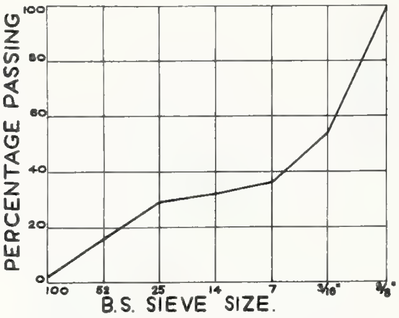

FIGURE 1: *Grading of aggregate.*

TABLE 2. *Mix details*

Maximum aggregate size is 3/8-in.

Mix	Aggregate-cement ratio	Water-cement ratio	Cement content	Compressive strength at 24 hr.	
				2 x 9¼-in. cylinder	3-in. cube
			lb/yd³	*psi*	*psi*
A	4	0. 35	760	4, 850	10, 250
B	4	. 40	750	4, 550	9, 550
F	4	. 45	740	4, 200	8, 850
G	4	. 55	730	3, 700	7, 550
J	6	. 55	520	3, 750	7, 600

Factors Affecting Creep

Age at Loading

One of the outstanding features of aluminous cement is its extremely rapid development of strength (see fig. 2). For this reason aluminous-cement concrete can be subjected to load at an age of 24 hr or even less, and it was therefore considered of interest to establish the creep characteristics of concretes loaded at different ages. Figure 3 shows the creep after a given time under load for concretes loaded between the ages of 18 hr and 11 days.

It can be seen that up to the age of about 2 days an increase in the age at loading results in a very considerable decrease in creep after any given time under load, and probably also in the ultimate creep. At later ages the influence of age at loading on creep becomes progressively smaller.

This behavior is interpreted to indicate the influence on creep of the degree of hydration of the cement paste, and it may be interesting to note that the creep-age at loading curve of figure 3 is very similar in form to a strength-age curve of figure 2 (the two curves being mirror images of one another).

In the past there was a tendency to explain the influence of age on creep in terms of the

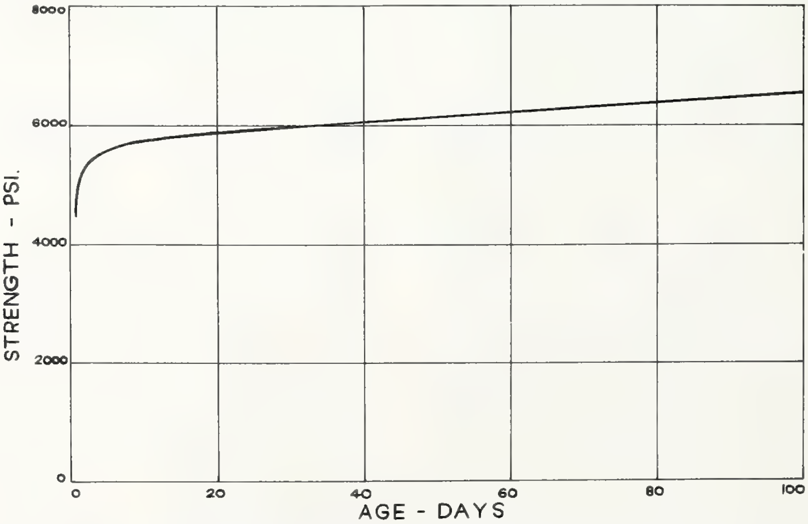

FIGURE 2: *Strength development of aluminous-cement concrete (mix A) stored at 95 percent rk; 2 by 9¼-in. cylinders.*

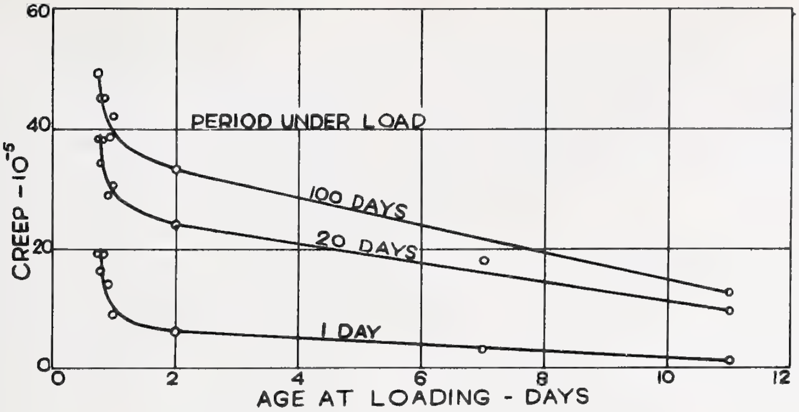

FIGURE 3: *Creep for different ages at loading.*
(Mix A, applied stress=2150 psi)

quantity of water available in the paste, but in the authors' opinion it is primarily the strength of the concrete at the time of application of the sustained load that affects the magnitude of creep. This influence of strength was established on the basis of tests on mortars differing only in the properties of the portland cement used [1]. Further evidence is given below.

Water-Cement Ratio

If, as suggested above, strength is the primary factor in creep, it would be expected that varying the strength of a mix by altering its water-cement ratio should be clearly reflected in the magnitude of creep. To check this hypothesis a series of mixes were made with values of the water-cement ratio between 0.35 and 0.55, the aggregate-cement ratio being kept constant at 4.0. All specimens were subjected to constant stress of 2,150 psi. The resulting relationship is most conveniently plotted as creep against $\frac{1}{\text{strength}}$, as an approximately straight line is then obtained (fig. 4). It is not thought, however, that a linear extrapolation into the range of higher strengths is justified: such a line would indicate a zero creep (after 100 days) for a strength of about 7,000 psi, while concrete of that strength would, of course, exhibit creep under the given load. It may be noted that the elastic strains on the application of the load, similarly plotted, also give a straight line which, if extended, would indicate no strain at approximately 6,500 psi. As mentioned before, such extrapolations are unwarranted, but the similarity between the elastic and creep curves is of interest.

In passing, it may be noted that, unlike the case of portland cement, the relation between the compressive strength of aluminous-cement concrete and the water-cement ratio is linear. This relationship is shown in figure 5 for the 2 by 9¼-in. cylinders of the present series and also for 3 by 9¼-in. cylinders made with the same cement as well as for standard 6 by 12-in. cylinders

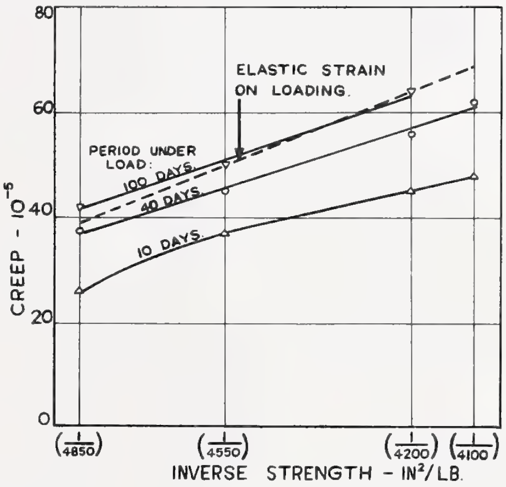

FIGURE 4: *The relation between creep and inverse strength at the time of application of load for mixes with different water-cement ratios.*
(Applied stress=2,150)

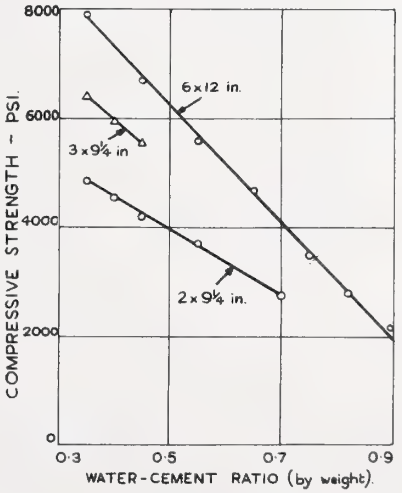

FIGURE 5: *The relation between 24-hr compressive strength and water-cement ratio for cylinders of different proportions.*

of another study, i.e., made with a different batch of aluminous cement.

Table 2 shows that the basic mixes had an aggregate-cement ratio of 4. Increasing this ratio to 6 (Mix J) has not affected the magnitude of creep, but pilot tests on much leaner mixes indicate that the aggregate-cement ratio may not always be disregarded.

Stress-Strength Ratio

In the present investigation, the majority of specimens were subjected to a sustained stress of 2,150 psi, this being the order of working stress for aluminous-cement concrete used, for instance, in a prestressed member. Only one series of specimens was used to check the relation between creep and stress, and this relationship was found to be linear, as is the case with portland-cement mortar and concrete. The stresses applied did not exceed 60 percent of the ultimate strength.

It is thus possible to express creep in terms of the ratio of the stress applied to the strength at the time of application of the load, or, in brief, the stress-strength ratio. Figure 6 shows a plot of the relevant data for the various specimens of the present investigation, and, for the limited range of variables involved, the significance level of this apparently linear relation is considerably better than 0.1 percent. It is clear, however, that this line would indicate no creep after 20 days under load for values of the stress-strength ratio below about 0.3. A similar pattern has been found for some tests of other investigators, as shown in an earlier paper [1].

The lower range of values of the stress-strength ratio has unfortunately not been investigated, as in the time available it was essential to concentrate on stresses and strengths used in practice. However, the behavior of concrete subjected to low stresses should be studied, particularly because a lowering of stress appears to decrease the creep less than a corresponding decrease in the stress-strength ratio obtained by an increase in strength. It is hoped to perform the necessary tests in the near future.

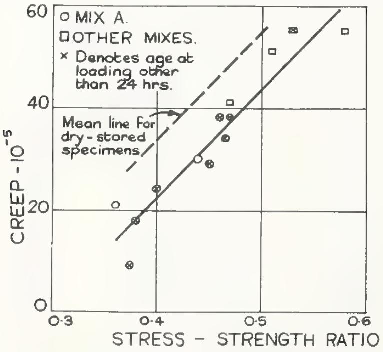

FIGURE 6: *The relation between creep after 20 days under load and the stress-strength ratio for wet-stored specimens.*
(Regression line shown)

Ambient Humidity

All the data presented so far referred to specimens stored at a relative humidity of 95 percent. Another series of tests was performed at a relative humidity of 32 percent and a temperature of 20 °C. The specimens were subjected to these dry conditions from the time they were stripped (at 24 hrs), and they exhibited, therefore, a considerable shrinkage. It was thus not possible for the specimens to achieve hygral equilibrium with the surrounding medium prior to the application of the load, so that some shrinkage-creep interaction was inevitable. Since, however, these conditions of early loading and simultaneous drying out are often encountered, it was considered worthwhile to obtain some test results, particularly in view of the belief, already mentioned, that the creep of aluminous-cement concrete in air is smaller than in water.

Under the circumstances it was necessary to distinguish between creep and shrinkage and, although the two are known not to be additive, there was no alternative but to subtract the shrinkage of unloaded companion specimens from the total-time deformation of specimens under load. (This makes the present results comparable in form with the older test results.) The resulting relation between creep and the stress-strength ratio is shown in figure 6, and it is clear that the creep of drying specimens stored at a relatively humidity of 32 percent is somewhat higher than that of humid specimens at 95 percent rh. After 20 days under load the difference was of the order of 0.0001 (strain), which represents an increase in creep of approximately 20 percent in a specimen with a stress-strength ratio of 0.5.

It appears then that the creep of a drying specimen is greater than the creep of humid specimens, and indeed this is the normal behavior of concrete made with portland cement. How then are Glanville's [3] results explained? It seems that his specimens were loaded at the age of 28 days, and their strengths at the time were 3,340 psi for the wet and 4,640 psi for the dry specimens. No explanation of this difference is available. If a loss of strength had occurred, the reason is not known, as the temperature was 10 °C [6]. It is also interesting to note that Glanville's data show an increase in the elastic strain with time for air-stored concrete. It is not clear whether this increase is related to a retrogression of strength.

In any case, taking the actual values of strengths at the time of application of the load, the creep should be adjusted in proportion to $\frac{1}{\text{strength}}$. It is more convenient to plot a product of creep and strength against time, and this relationship is shown in figure 7. It can be seen that, on this basis, there is very little difference between the creeps of dry and wet specimens, although at periods under load greater than 14 days the latter show a slightly higher creep. It should be remembered that in Glanville's investigation the load was applied at the age of 28 days, so that the pattern of shrinkage development was possibly quite different from that in the present experiments.

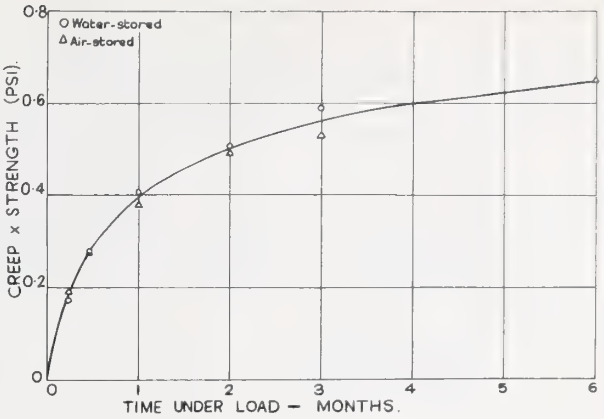

Figure 7: *Creep times strength for Glanville's* [3] *air- and water-stored aluminous-cement concrete.*

Creep Recovery

Upon release of load the specimens of aluminous-cement concrete exhibited an instantaneous recovery corresponding to the modulus of elasticity of concrete at that time, and this elastic recovery was followed by a gradual creep recovery. These movements are similar to those characteristic of portland-cement concrete, and in particular the very rapid completion of creep recovery can be observed. Figure 8 shows a typical deformation-time curve for mix A specimens loaded at 18 hr to a stress of 2,150 psi; both the creep and the creep-recovery are shown.

No clear trend in the values of the creep recovery has been observed. It can, therefore, be tentatively concluded that creep recovery is not a simple function of the strength of concrete, but the factors influencing it have not been recognized. As a corollary, it would appear that the nature of creep recovery is not necessarily the same as that of creep; a similar conclusion was drawn in the case of portland cement mortars [2].

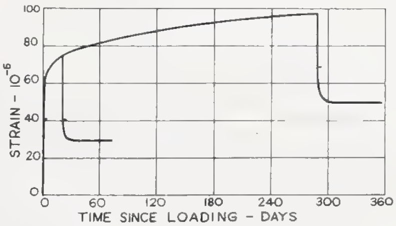

Figure 8: *Elastic strain, creep, and creep recovery for mix A under 2,150 psi.*

Comparison With Portland Cement

In a previous investigation [1] of creep of mortars made with portland cements of different compositions, one mortar made with aluminous cement was included, and in a comparison on the stress-strength basis there was no apparent difference between the two types of cement. In the present tests a few check mixes made with rapid-hardening portland cement (Type III) again showed that on the basis of the stress-strength ratio at the time of application of the load, the creep of concretes made with the two cements appears to be of the same order of magnitude, although the actual values are affected by the varying rates of strength development of the two cements. This lack of an inherent difference between the creeps of portland and aluminous cements is of considerable interest in the study of the nature of creep; it would appear to be at variance with Bernal's [7] suggestion that creep is related to the movement of zeolitic water in calcium silicate hydrates. Since the products of hydration of aluminous cement and of portland cement are largely dissimilar, it is much more likely that creep is related to the grosser structure of the cement gel—a suggestion supported by Powers [8], and intimated in an earlier study [1].

Summary and Conclusions

Although the tests reported here cover only a limited field, they are the first set of data on the creep of aluminous-cement concretes of different mixes, and thus enable us to obtain a general picture of the behavior of that cement.

The age at loading appears to affect very strongly the magnitude of creep after any time under load and probably also the magnitude of the ultimate (limiting) creep. This influence is particularly strong at ages below about 2 days: by delaying the application of the load from the age of 18 to 48 hr creep can be reduced by about one-third. The magnitude of creep appears to be related inversely to the strength of concrete at the time of application of the load.

A similar relation is found when the strength of concrete is varied by a change in the water-cement ratio for a constant cement content. There is thus a linear relation between creep and the inverse of strength over the range of strength values investigated: this relationship covers water-cement ratios between 0.35 and 0.55, and would correspond to 24-hr strengths of standard 6 by 12-in. cylinders between about 5,500 and 8,000 psi.

It is possible thus to express creep as a linear function of the stress-strength ratio, but for values of this ratio below about 0.3 the behavior is not clearly established. It is likely that, as suggested by Evans [9], another relation exists in the lower range of stress-strength ratios; there are some indications of this from specimens subjected to low stresses.

The ambient humidity has been shown to affect creep comparatively little, the creep of drying specimens being somewhat higher than the creep of wet-stored concrete. This is in agreement with the pattern of behavior of portland-cement concretes but directly opposite to previous results on aluminous-cement concrete [3]. This apparent anomaly is explained by the very much higher strength of dry specimens as compared with humid specimens in those earlier tests. The clarification of this point is believed to be of considerable interest.

The pattern and magnitude of creep and of creep recovery of aluminous-cement concrete appear to be similar to those of concretes made with portland cements. Since the chemical compositions of the products of hydration of the two basic types of cement are largely different, it can be inferred that creep is related to the grosser structure of the hydrated paste rather than to the crystal structure of calcium silicate hydrates. The close relation between creep and strength can be interpreted to mean that the gel-space ratio, established by Powers [10], is a primary factor in creep. The mechanism of creep is likely to be bound up with the volume of pores not filled by the hydrated cement paste: a further investigation of this physical aspect of concrete is essential in improving our knowledge of the engineering properties of this material.

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Paper V-S2. Strength, Elasticity, and Creep as Related to the Internal Structure of Concrete*

Torben C. Hansen

Synopsis

On the basis of that conception of the microstructure of cement paste which has recently been presented by Powers, Grudemo, and others, it has been possible to derive an interrelation between the elasticity of cement paste and concrete and the gel space ratio or gel density (as defined by Powers). When applied to concrete, an approximate theoretical interrelation between strength and elasticity is obtained which is in good agreement with experimental results.

Following the same lines the two components of creep, delayed elasticity and viscosity, could be related to the gel density at any age of the cement paste, and to the volume concentration of cement paste in concrete. Even the effect of the time under sustained loading could be taken into consideration when applying certain standard time functions for the two components of creep (established on the basis of a rheological model).

The sum of the theoretical terms for delayed elasticity and viscosity gave the final creep equation for concrete, not exposed to any drying or wetting during the time of sustained loading. It has been shown that the creep calculated according to this equation is in good agreement with the creep determined in 42 creep tests found in the literature. The general creep equation which is based on our knowledge of the internal structure of cement paste can be directly applied for a practical calculation of the creep of any water-stored concrete, cement mortar, or cement paste, under the above-mentioned conditions when the age at loading, the time under sustained loading, the chemical composition of the cement, and the composition of the concrete (water-cement ratio and volume concentration of cement paste) are known.

Résumé

En s'appuyant sur la conception de la microstructure de la pâte de ciment—laquelle a été récemment présentée par Powers, Grudemo, et par d'autres auteurs—, il a été possible de dériver une interrelation entre l'élasticité de la pâte de ciment et du béton, et le "gel-space ratio" ou "gel density" (comme le définit Powers). Quand on l'applique au béton, on obtient une interrelation théorétique approximative entre la résistance et l'élasticité, qui est en bon accord avec les résultats expérimentaux.

Suivant les mêmes idées, on pourrait établir un rapport entre (1) les deux composants du fluage: l'élasticité retardée et la viscosité, et (2) le "gel density" de la pâte de ciment à l'âge choisi et la concentration volumétrique de la pâte de ciment dans le béton. On pourrait même tenir compte de l'effet du temps pendant la charge de longue durée quand on applique certaines fonctions de temps pour les deux composants du fluage (établies sur la base d'un modèle rhéologique).

La somme des expressions théorétiques pour l'élasticité retardée et la viscosité donnèrent l'équation finale du fluage pour le béton qui n'est pas exposé au séchage ni au mouillage pendant la période de charge de longue durée. Il est démontré que le fluage calculé suivant cette équation est en bon accord avec le fluage déterminé par 42 essais de fluage trouvés dans la littérature. Cette équation générale du fluage, qui est basée sur notre connaissance de la structure interne de la pâte de ciment, peut être utilisée directement dans le calcul pratique du fluage de tout béton, mortier et pâte de ciment conservés dans l'eau sous les conditions mentionnées ci-dessus, quand on connaît l'âge à la mise en charge, la période de charge de longue durée, la composition chimique du ciment et la composition du béton, c'est à dire le rapport eau-ciment et la concentration volumétrique de la pâte de ciment.

Zusammenfassung

Auf der Grundlage des Begriffs der Zementpastenmikrostruktur, wie er neulich von Powers, Grudemo und anderen Forschern ausgearbeitet worden ist, bekam es möglich, eine Beziehung zwischen der Elastizität der Zementpaste und des Betons und dem Gel-Volumen-Verhältnis oder Geldichte, wie von Powers definiert wurde, aufzustellen. Wenn man diese für Beton anwendet, bekommt man eine ungefähre theoretische Beziehung zwischen Festigkeit und Elastizität, die mit den experimentellen Ergebnissen gut übereinstimmt.

Durch Weiterentwicklung dieses Begriffs war es möglich eine Beziehung zwischen den beiden Kriechkomponenten, d.h. der verzögerten Elastizität und der Viskosität, und der Geldichte für jedes Alter der Zementpaste, und auch der Volumenkonzentration der Zementpaste im Beton aufzustellen. Auch die Zeitwirkung bei fortgesetzter Belastung konnte erklärt werden, wenn gewisse genormte Zeitfunktionen für die zwei Kriechkomponenten, wie sie von einem rheologischen Modell abgeleitet worden sind, angewandt werden.

Die Summe der theoretischen Ausdrücke für die verzögerte Elastizität und die Viskosität lieferte die endgültige Kriechgleichung für Beton, wenn dieser während der Zeit der ununterbrochenen Beladung keinem Trocknen oder keiner Naßmachung ausgesetzt ist. Es

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden. (The author was with the Portland Cement Association, Skokie, Illinois, at the time of the Symposium.)

wurde gefunden, daß das Kriechen, wie sie nach dieser Gleichung berechnet wurde, vorzüglich mit dem Kriechen, das in 42 Kriechprüfungen in der Literatur beschrieben worden ist, übereinstimmt. Die allgemeine Kriechgleichung, welche von der Kenntnis der inneren Struktur der Zementpaste abgeleitet worden ist, kann direkt auf das Kriechen unter praktischen Bedingungen eines jeden unter Wasser aufbewahrten Betons, eines Zementmörtels und einer Zementpaste angewandt werden, wenn die obigen Bedingungen erfüllt sind; man muß als Parameter die Zeit der ununterbrochenen Beladung, die chemische Zusammensetzung des Zements und die Betonzusammensetzung, d.h. das Verhältnis Wasser / Zement und die Volumenkonzentration der Zementmasse, kennen.

Introduction

For many years concrete research has dealt with engineering aspects, that is, so to say, with the external behavior of the material when loaded in different ways or exposed to various conditions. Very little has been known about the internal mechanism which is the basis of the external behavior of concrete. However, our knowledge concerning the physical structure of cement paste and concrete increases, and a gap has quickly developed between the physical discoveries and the engineering aspects. In this paper the author has tried to relate certain external phenomena to the internal structure of concrete, and thus bridge that gap.

The Microstructure of Cement Paste

Basic studies of the physical chemistry of hardened cement paste have established that the structure of paste is an agglomeration of unhydrated grains of cement which are joined by an aggregation of colloid or microcrystalline particles, the so called cement gel.

Electron-micrographs obtained by Grudemo [1] [1] in the laboratories of the Portland Cement Association revealed to some extent the physical mechanism of the hydration of cement. Grudemo found that when cement grains start hydrating, a coarsely fibrous structure of slender rods grows radially from the grains into the outer solution. In the areas of contact between cement particles the rodlike formations grow in between each other and bonds are formed by superposition of the atomic structure in the contact areas, this probably causing the first binding in the cement paste. Subsequently the rodlike or partly fibrous elements gradually grow out to fill all the interstitial spaces, and simultaneously a steadily increasing number of bonds are formed in the areas of intersection between them. The bonds in these contact points are probably one of the sources of strength and rigidity of cement paste.

The formation of an increased amount of colloidal material on the surfaces makes the interior parts of the cement grains less easily accessible to attack by the outer solution, thus leading to a decrease in the rate of hydration. The slowing up of the process of hydration seems to produce conditions favorable for the generation of another component which is composed of a felted mass of extremely thin wrinkled foils. In the second stage of hydration in ordinary paste, this component grows out, in the course of time filling all meshes in the network formed by the coarsely fibrous structural elements. On account of the cohesive forces in the network, this mass finally becomes so strongly compressed that its character of a layer structure is no longer discernible. In this way a stationary third stage is reached in which all possible changes proceed at a very slow rate.

The strength as well as the deformational properties of cement paste and concrete is probably determined by the molecular structure in the surfaces of these colloidal particles and the bond between them.

Strength and Elasticity

Strength as Related to the Internal Structure of Concrete

Both the rodlike structure and the felted mass probably contribute to the strength and rigidity of cement paste. If this is true, three different stages should be observed when strength is plotted against age of cement paste or concrete. P. G. Hansen [2] found that the graph of strength versus age of concrete plotted logarithmically shows the strength-age curve from 0 to about 30 hr as a straight line, from 30 to 72 hr as another straight line and from 72 hr to 28 days as a still different straight line (see fig. 1). These time intervals are in accordance with Grudemo's observations of the different stages of hydration.

Reinius [3] developed a theory which gives an explanation of the mechanism of short-time deformation and failure of concrete on the basis of a mechanical model of cement paste which is principally in accordance with Grudemo's observations.

It was suggested that the force acting upon a concrete specimen is transmitted from particle

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[1] Figures in brackets indicate the literature references at the end of this paper.

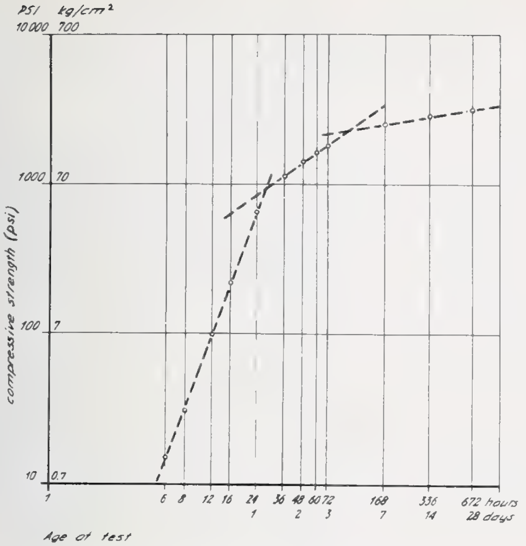

FIGURE 1. *Graph of ultimate compressive stress vs. age of concrete showing the three stages of hydration.*

(Experimental data obtained by P. G. Hansen [2].)

to particle by a lattice of more or less needle-shaped crystals. Some of the crystals are oriented in the direction of the acting load and some are inclined and try to push the particles aside. Other crystals, perpendicular to the direction of the load, hold the particles together by tension. The elongation of these crystals results in a lateral expansion when the concrete is subjected to axial compression.

Since the tensile strength of the crystal lattice structure is much less than the compressive strength, a progressive fracture starts when the tensile strength of the crystals perpendicular to the applied load is reached. The weak crystals fail first, and the stronger at greater loads, and tension cracks appear parallel to the load, as observed when concrete cubes or cylinders are loaded and the friction at the end surfaces is eliminated.

Reinius suggested that the bond of needle-shaped crystalline cement gel particles between two unhydrated grains of cement, as well as the bonds between grains of aggregate, could be replaced schematically by two bars in the plane of the force. As a result of an extensive theoretical analysis of this mechanical model of concrete, Reinius was able to explain not only the nature of rupture and crack formation in concrete under different types of load, but also the deformational behavior up to rupture, the variation of Poisson's ratio under increasing load, etc.

Reinius' theory is restricted to the mechanism of deformation and strength, and does not take into account the influence of the composition of concrete on these properties. However, our present knowledge concerning the physical structure of the material is sufficient to extend the theory and take these factors into account.

An increase in the water content of concrete increases the distance between cement grains in the paste, and therefore decreases the number of welding points and gel connections between unhydrated grains of cement. Since the strength as well as the rigidity depends on the number of such connections, strength decreases and short-time deformations increase with increasing water content, that is to say with increasing water-cement ratio.

It is reasonable to believe that strength as well as rigidity is proportional to the degree of hydration of cement paste, since a certain change in hydration means the formation of a certain amount of new gel (Powers and Brownyard [4]) and thus a certain amount of new connections and contact points between unhydrated cement grains.

It is remarkable the Grudemo [1] found that even large variations in the mineral composition of cement do not cause substantial changes in the microstructural composition of the final product. Powers, Mann, and Copeland [5] later stated that the specific surface of the hydration products only varies little with the chemical composition of the cement, thus indicating that these products are the same for all cements. Therefore it may be expected that the strength and rigidity are not influenced by the type and composition of the cement in any other way than through the amount of gel formed per degree of hydration.

Consequently the strength and rigidity of concrete should depend on the water content and the age in the following way

$$F_c = f\left(\frac{V_{hc}}{w_o}\right)$$

where F_c=strength of cement paste, mortar or concrete; V_{hc}=total volume of the gel (depending on the type of cement and the age); w_o=weight of original water content after bleeding.

Powers and Brownyard [4] showed empirically that the strength of cement mortar is approximately proportional to the gel space ratio, i.e.,

$$\frac{\text{volume of gel}}{\text{original space available for the increase in volume of gel phase}} = \delta\,\frac{V_m}{w_o} = \delta\,\frac{k w_n(t)}{w_o}$$

where V_m=constant, proportional to the surface area of the gel, w_o=weight of original water content after bleeding, g/cc, $w_n(t)$=weight of non-evaporable water, g/cc, k=constant, characteristic of the cement. k is related to the computed compound composition as follows: $k = 0.230\ (C_3S) + 0.320\ (C_2S) + 0.317\ (C_3A) + 0.368\ (C_4AF)$ where the symbols in parentheses represent the computed weight proportions of the compound indicated. δ=proportionality factor between V_m and total volume of gel V_{hc}.

In a later paper Powers [6] reported that the strength of cement mortar more correctly is a function of another ratio or what we may call the gel density V_5.

$$V_5=\frac{V_{hc}}{V_{hc}+p_c}$$

where V_{hc}=volume of gel; p_c=volume of capillary pores.

Powers found that the strength F_c could be represented by the expression

$$F_c \cong a V_5^d. \tag{1}$$

Both a and the order of V_5 vary somewhat from cement to cement.

When considering the strength of concrete, some other factors are also of importance, such as the quality and grading of the aggregate material, and the bond between aggregate and cement paste. Therefore eq (1) will only apply as a very rough approximation.

Elasticity as Related to the Internal Structure of Concrete

It has been suggested by the author [7] that the internal structure of a heterogeneous material like concrete can be built up in two quite different ways.

The *ideal combined hard material* has a continuous lattice of an elastic component with a high modulus of elasticity, and the voids are filled up with another component with a lower modulus of elasticity.

The *ideal combined soft material* has grains of an elastic component with a high modulus of elasticity embedded in a continuous component with a lower modulus of elasticity.

The author has derived fundamental equations for calculating the moduli of elasticity of the two types of structures when the moduli of elasticity of the components and their volume concentrations are known.

For a *combined hard material* the modulus of elasticity can be calculated from the assumption that the strain is the same over a whole cross section.

Let a material of this type be represented by a unit volume (see fig. 2) composed of two parallel columns consisting of a hard and a soft component. The modulus of elasticity for the material can then be calculated as follows:

$$\epsilon=\frac{\sigma_s}{E_s}=\frac{\sigma_h}{E_h} \tag{2}$$

where ϵ=elastic strain of the combined material; E_s=the modulus of elasticity for the soft component; E_h=the modulus of elasticity for the hard component; σ_s=stress on the soft component; σ_h = stress on the hard component.

Since the sum of the forces over the section must equal the total external force $\sigma\cdot 1$

$$\sigma_s V_s+\sigma_h V_h=\sigma\cdot 1 \tag{3}$$

where V_s=area of cross section of column consisting of soft material=volume concentration of the soft component; V_h=area of cross section of column consisting of hard material=volume concentration of the hard component.

From eqs (2) and (3)

$$\frac{\epsilon E_s V_s}{\epsilon}+\frac{\epsilon E_h V_h}{\epsilon}=\frac{\sigma}{\epsilon}=E$$

or the fundamental equation for a *combined hard material:*

$$E=V_s E_s+V_h E_h \tag{4}$$

where E=modulus of elasticity for the combined material, E_s=modulus of elasticity for the soft component, E_h=modulus of elasticity for the hard component.

For a *combined soft material* the modulus of elasticity can be calculated from the assumption that the stress is the same over a whole section.

Let a material of this type be represented by a unit volume (see fig. 3) composed of two layers consisting of the hard and the soft component. The modulus of elasticity can then be calculated as follows

$$\epsilon_s V_s+\epsilon_h V_h=\epsilon\cdot 1 \tag{5}$$

where V_s=depth of layer consisting of soft material=volume concentration of the soft com-

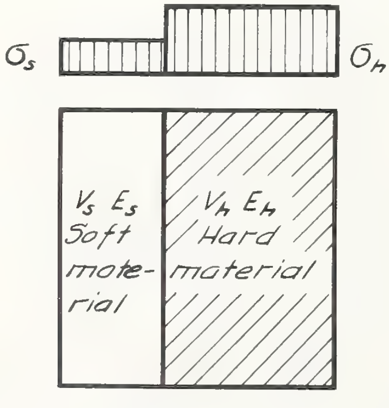

FIGURE 2. *Stress distribution over a unit volume of a combined hard material.*

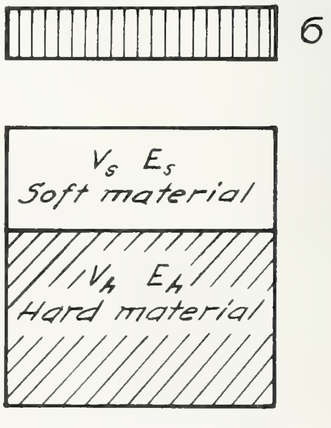

FIGURE 3. *Stress distribution over a unit volume of a combined soft material.*

ponent, V_h=depth of layer consisting of hard material=volume concentration of the hard component, ϵ_s=strain of soft component, ϵ_h=strain of hard component.

$$\epsilon_s=\frac{\sigma}{E_s} \tag{6}$$

and

$$\epsilon_h=\frac{\sigma}{E_h}. \tag{7}$$

By substituting eqs (6) and (7) in eq (5)

$$\epsilon=\frac{\sigma V_s}{E_s}+\frac{\sigma V_h}{E_h}=\frac{\sigma}{E}$$

or the fundamental equation for a *combined soft material:*

$$E=\frac{1}{\frac{V_s}{E_s}+\frac{V_h}{E_h}} \tag{8}$$

where all symbols are the same as the ones used in the previous calculation of the modulus of elasticity for a *combined hard material.*

Generally, cement paste or mortar is the continuous component in concrete while the stone particles are embedded in this mass. If the modulus of elasticity of the stones is higher than that of the mortar, as in most cases, it is possible to calculate the modulus of elasticity of concrete from the moduli of elasticity of the components and their volume concentrations on the assumption that concrete is a combined soft material, that is from the following equation:

$$\frac{1}{E}=\frac{V_1}{E_1}+\frac{V_2}{E_2} \tag{9}$$

where V_1=volume concentration of cement paste or mortar in concrete, V_2=volume concentration of aggregate in concrete, E=modulus of elasticity of concrete, E_1=modulus of elasticity of cement paste or mortar, E_2=modulus of elasticity of aggregates.

This has been done by the author in table 1 (experiments 1–27) on the basis of the experimental results of Dantu [8] and La Rue [9].

If, however, the modulus of elasticity of the stones is lower than that of mortar, then the modulus of elasticity should be calculated on the assumption that concrete is a combined hard material or from the following equation:

$$E=V_1E_1+V_2E_2 \tag{10}$$

where all symbols are the same as used above.

This has been done by the author in table 1 (experiments 28–30) on the basis of the experimental results of La Rue [9].

It will be seen that there is excellent agreement between the calculated and the experimentally determined moduli of elasticity (see table 1, column 11). Only in experiment 16 is the agreement not so good. This is due to the fact that the glass balls here are very densely packed. The volume concentration is 64 percent. The most dense packing gives a volume concentration of 74 percent. The glass balls are so densely packed that many of them must touch each other and thus we are in a transition zone between a combined soft and a combined hard material. As a matter of fact, in a real material some embedded particles will always touch each other. Therefore the experimentally determined moduli will generally lie between the results obtained by the two ideal equations (see table 1, columns 8, 9, and 10). In most cases there will be no doubt, however, as to which group a material should be assigned.

The author has tried to analyze the behavior of the cement paste according to the same principles.

The cement paste is to be regarded as a combined soft material consisting of hard grains of unhydrated cement embedded in a continuous soft component of cement gel and pores. The modulus of elasticity of cement paste can therefore be determined from eq (11),

$$\frac{1}{E_1}=\frac{V_3}{E_3}+\frac{V_4}{E_4} \tag{11}$$

where V_3=volume concentration of gel and capillary pores in cement paste, V_4=volume concentration of unhydrated cement grains in cement paste, E_3=modulus of elasticity of gel and pores, E_4=modulus of elasticity of unhydrated cement grains.

The phase consisting of gel and pores is to be regarded as a continuous hard material and the modulus of elasticity can therefore be determined from the following equation:

$$E_3=V_5E_5+V_6E_6=V_5E_5 \tag{12}$$

where V_5=volume concentration of gel in the component consisting of gel and capillary pores; V_6=volume concentration of pores in the component consisting of gel and capillary pores, E_5=modulus of elasticity of cement gel, E_6=modulus of elasticity of capillary pores=0.

By substituting eqs (11) and (12) in eq (9) we get *the fundamental equation*

$$\frac{1}{E}=\frac{V_3V_1}{V_5E_5}+\frac{V_1V_4}{E_4}+\frac{V_2}{E_2} \tag{13}$$

from which it should be possible to determine the modulus of elasticity of concrete when the moduli of elasticity and the volume concentrations of components are known.

Grudemo [1] found that even large variations in the mineral composition of cement do not cause

Table 1. *Comparison between calculated and experimentally determined moduli of elasticity for some heterogeneous materials*

1	2	3	4	5	6	7	8	9	10	11
Exp. no.	Source	Aggregate	Mortar	$V_2=$ vol. % agg.	$E_{2(\mathrm{agg})}$ kg/cm² × 10^{-3}	$E_{1(\mathrm{mortar})}$ kg/cm² × 10^{-3}	E_{exp} for concrete kg/cm² × 10^{-3}	$E'_{\mathrm{calc}}=\frac{1}{\frac{V_1}{E_1}+\frac{V_2}{E_2}}$ kg/cm² × 10^{-3} soft material	$E''_{\mathrm{calc}}=V_1E_1+V_2E_2$ kg/cm² × 10^{-3} hard material	$\frac{E_{\mathrm{exp}}}{E'_{\mathrm{calc}}}$ or $\frac{E_{\mathrm{exp}}}{E''_{\mathrm{calc}}}$
1	Dantu [8]	20–40 mm Diorite	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	0. 40	1, 041	346	495	475	624	1. 04
2				. 50	1, 041	346	550	520	694	1. 05
3				. 55	1, 041	346	568	548	728	1. 04
4		10–20 mm Diorite	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	. 33	1, 041	337	425	433	575	0. 98
5				. 42	1, 041	337	471	471	638	1. 00
6				. 52	1, 041	337	527	520	707	1. 01
7		10–20 mm Diorite	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	. 33	1, 047	326	419	421	564	1. 00
8				. 42	1, 047	326	475	459	629	1. 04
9				. 52	1, 047	326	518	509	701	1. 02
10		Glass spheres 17–18 mm Ø	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	. 35	742	313	399	393	463	0. 99
11				. 45	742	313	431	422	506	1. 02
12				. 55	742	313	467	458	549	1. 02
13		Pieces of glass 12.5–22 mm	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	. 35	742	313	393	392	463	1. 00
14				. 45	742	313	426	422	506	1. 01
15		Steel cylinders 5 mm Ø h=5 mm	Cement 700 kg/m³ Sand 1,260 kg/m³ Water 300 kg/m³	. 55	2, 200	313	600	592	1, 350	1. 01
16		Glass spheres 5 mm Ø	Araldite	. 64	720	39	175	99	475	1. 57
17		10–20 mm Diorite	Gypsum	. 59	1, 047	374	638	602	771	1. 06
18		Steel balls 5 mm Ø	Alliage-lino	. 54	2, 200	289	650	545	1, 320	1. 19
19	LaRue [9]	Limestone (Plattin) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	. 43	795	374	485	484	557	1. 00
20				. 47	795	374	529	499	572	1. 06
21				. 52	795	374	472	519	592	1. 10
22		Limestone (Burlington) (RM Carthage) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	. 43	632	374	417	454	486	0. 92
23				. 47	632	374	411	464	496	0. 89
24				. 52	632	374	465	478	507	0. 97
25		Limestone (Burlington) (LM Carthage) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	. 43	473	374	356	411	417	0. 87
26				. 47	473	374	347	415	420	0. 84
27				. 52	473	374	399	422	425	0. 94
28		Limestone (Bowling Green) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	. 43	131	374	272	222	268	1. 01
29				. 47	131	374	275	199	258	1. 07
30				. 52	131	374	284	192	248	1. 14

substantial changes in the microstructural composition of the cement gel. Therefore it may be expected that the modulus of elasticity of the gel component is rather constant and independent of the type and composition of the cement used.

A Relationship Between Strength and Elasticity

Powers [6] showed that the following relationship exists between strength of mortar F_c and gel density of cement paste,

$$F_c=aV_5^d$$

where a can vary between large limits with the type of cement used. However,

$$a\sim 1{,}160 \text{ kg/cm}^2$$

is a reasonable average value. The value of d can vary somewhat from cement to cement, but for an average cement we get:

$$d\sim 2.5.$$

When applying the following average values for concrete, $E_5=300{,}000$ kg/cm², $E_2=600{,}000$ kg/cm², $V_1=0.3$, $V_2=0.7$, $V_3=1.0$, $V_4=0.0$, we get from eq (13):

$$E=\frac{1}{\frac{V_1}{V_5E_5}+\frac{V_2}{E_2}}=\frac{1}{\frac{0.3}{300{,}000V_5}+\frac{0.7}{600{,}000}}=\frac{600{,}000}{\frac{0.6}{V_5}+0.7}. \tag{14}$$

By substituting eq (14) in eq (1) we get the following approximate relationship between strength and modulus of elasticity of an average concrete:

$$E=\frac{600{,}000}{0.6^{-2.5}\frac{F_c}{1{,}160}+0.7}.$$

From figure 4 it is seen that this relationship covers reasonably well the experimental results obtained by Roš [10] and C.U.R. [11].

The apparent correlation between modulus of elasticity and strength of concrete, which has so often been observed, is explained by the fact that both properties depend on the gel density.

The large scatter of the experimental results around the theoretical curve in figure 4 is probably due to the actual variation in type of cement, modulus of elasticity of aggregates, volume concentration of cement paste, and other factors which have been regarded as invariables for different concretes when establishing eq (1) and eq (14).

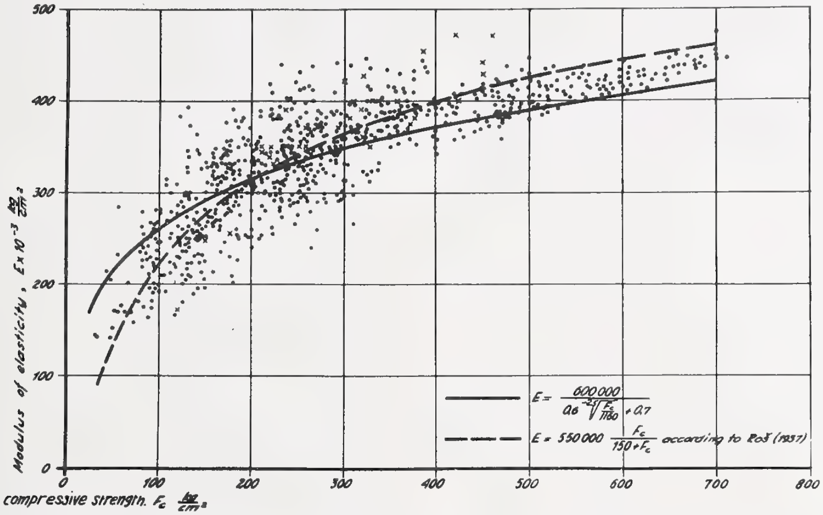

FIGURE 4. *Graph showing theoretical and experimental correlation between strength and modulus of elasticity of concrete.* (The experimental data have been collected by Roš [10] and C.U.R. [11].)

Creep

The Internal Mechanism of Concrete Creep

According to Flügge [12], Reiner [13], and T. C. Hansen [7], the viscoelastic behavior of concrete can be described by means of a rheological model, a Burgers body as shown in figure 5, where the four rheological constants vary with the age of concrete.

A rheological model is a combination of ideal elastic and viscous elements in series or parallel, which represents the behavior of actual materials under load or deformation.

The element E_M describes the instantaneous elastic deformation of concrete, λ_M the viscous part of creep; E_K and λ_K in series describe the delayed elastic part of creep.

It should be emphasized that the use of this model is to give a phenomenological description of the viscoelastic response of concrete, but it does not necessarily imply anything about the molecular mechanisms responsible for the observed behavior. Several attempts have been made to develop a molecular theory of viscoelastic behavior of concrete, but no theory is commonly accepted. During the last few years our knowledge of cement paste has been extended so far that it should be possible to give at least a tentative explanation of creep.

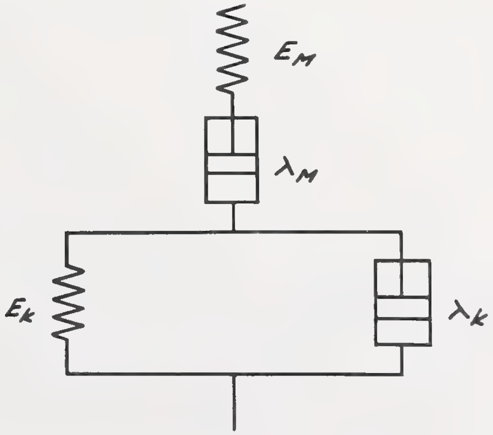

FIGURE 5. *Suggested rheological model for concrete.*

Cement gel shows a remarkable structural stability as compared with other hydrogels, when exposed to external load or to changes in moisture content and consequential shrinkage or swelling. According to Grudemo [1] the principal cause of this dimensional stability is to be sought in the presence of the framework of fibrous particles. It can be presumed that the units of this framework have a comparatively great flexural rigidity on account of their tubular structure.

The more amorphous part of cement gel, the felted structure of crumpled sheets and foils, probably contains the main part of the absorbed water after the cement has hardened. The number of gel particles is about 7 x 10^{16} per cc, and the interstitial spaces are therefore minute. They are of the order of a few molecular diameters. When two particles are in such proximity, they exert a mutual attraction, the "van der Waals" forces. When the paste is thoroughly dried out, the van der Waals forces and, to some extent, chemical bonds are the only bonds between the gel particles. When the paste is wetted, the water molecules spread all over the gel surface because of mutual attraction between them and the molecules composing the solid surface. The water molecules act against the above-mentioned bonds between adjacent surfaces, thus forcing the surfaces apart and weakening the bonds. The result of the wetting is a swelling and a reduced strength compared with that of dry paste. When the paste dries, the water evaporates and the paste shrinks.

Creep of concrete is a sum mainly of two different types of deformation, the viscous time-dependent deformation and the delayed elasticity. Grudemo [1] has suggested that these deformations take place as lateral or angular displacements in the points of intersection of the gel framework of the cement paste.

It was mentioned earlier that the bonds between the solid gel particles probably are van der Waals forces, hydrogen bonds, and chemical bonds. The author suggests that the viscous deformation of cement paste is a viscous flow in the grain boundaries or welding points. While the van der Waals forces as well as the hydrogen bonds are forces of the same type as the forces which hold the molecules of a liquid together, there has been some doubt whether solid bonds like chemical or crystalline bonds can behave in a viscous manner. Usually dislocations and consequential plastic deformation properties are attributed to solid bonds. However, lately Kê [14, 15, 16] has shown that the grain boundaries in polycrystalline metals, where the atom positions represent a compromise between the crystalline arrangements in two adjoining grains, can behave in a viscous manner. Hence cement gel is not unique in showing viscous flow in grain or particle boundaries. It is recognized, however, that time-dependent permanent set due to collapse of the gel structure, when submitted to a sustained load, may also contribute somewhat to the nonreversible part of creep. This may be the case specially when concrete is exposed to simultaneous drying or wetting.

So far, no theory has been presented which can conclusively explain the delayed elastic part of creep. However, the retardation of deformation in solid materials is often thought to be due to internal diffusion processes.

The cement paste consists of a solid network of particles which are loosely linked and may be capable of orientation. The response of this structure to stress is probably diffusion controlled, and molecular orientation is induced by stress due to external load. This means that a less probable state is induced by the application of stress. The configurational entropy is decreased so that release of stress results in an attempt by the molecules to restore maximum entropy and hence produce a definite restoring force.

The sources of delayed elasticity of concrete are probably the same, in the main, as in glass (Douglas [17]). In addition to a chemical diffusion, a certain amount of segmental diffusion of the solid particles, the slender ribbons and the crumpled sheets and foils, might occur. Each individual chain molecule, or whole conglomerations of molecules of the intertwined assembly, wriggle around from one configuration to another. The higher the temperature, the faster is this diffusional motion. When a stress is imposed on the system, this intermolecular Brownian motion is biased, and oriented molecular configurations are favored. When the load is released, the segments will tend to return to the original positions and the retardation will be the same on unloading as during the time of sustained loading.

The new equilibrium distribution of configurations (under stress) due to chemical and segmental diffusion corresponds to the equilibrium elastic strain of the delayed elasticity. The retardation time is determined by the rate of the diffusional motion.

It has been suggested by other authors that the water molecules absorbed on the surfaces of the gel particles will start moving from the more-stressed areas to less-stressed areas when an external load is applied on cement paste. When the stress is released, the water tends to return to the original position. The result is a complete recovery unless the internal structure has in some other ways been modified by the sustained load. It is an important objection against this theory that no exchange of water takes place between a concrete specimen and the surroundings, due to sustained loading. It has been possible to prove neither that a large scale migration of water molecules takes place within the cement paste after application of an external load, nor that the internal relative humidity is altered when the external load is applied. If such a migration really occurs, it does not seem to imply any disturbance in the moisture equilibrium of the concrete but only a movement of gel water from one location to another.

In an earlier paper the possible relations between creep and shrinkage were discussed (T. C. Hansen [7]).

It was concluded that some process in connection with the water diffusion during the period of drying influences the creep properties of concrete. Therefore, it is believed that there is an interrelation between creep and shrinkage. These two concrete properties are probably both influenced by a common process taking place in the concrete during the period of drying. But it is not necessarily true that the shrinkage in itself influences creep or vice versa.

To avoid the effect of this interdependence between shrinkage and creep, when experimentally studying creep, the concept of "basic creep" was introduced. Basic creep was defined as creep of concrete which is not exposed to any moisture diffusion and consequential shrinkage or swelling during the period of sustained loading. Since the effect of drying and wetting severely influences the experimental results, a connection between creep and the factors influencing creep (other than drying and wetting, see table 2), is more likely to be revealed if basic creep is investigated, than when creep of drying concrete is determined.

Table 2. *The internal primary variables for basic creep*

1. The cement quality.
2. The water-cement ratio.
3. The quantity of cement paste in the concrete.
4. The rheological properties of the aggregates.
5. Admixtures.
6. The intensity of the compaction process.
7. The type and importance of load.
8. The stage of hydration of the cement paste when load is applied.
9. The temperature.

Theoretical Equation Relating Basic Creep of Concrete to Water-Cement Ratio, Volume Concentration of Cement Paste, Type of Cement, Age at Loading and Time Under Sustained Loading

It is reasonable to believe that the modulus of viscosity λ_M as well as the delayed elastic modulus of concrete E_K increases with the amount of cement gel formed. The two moduli must also increase with decreasing distance between the cement grains, that is, with decreasing water-cement ratio. Thus it appears that the same factors influence the strength and elasticity of cement paste as well as the deformations under sustained load.

It is not obvious that the gel density which proved to be a useful parameter when dealing with strength and elasticity should also apply for creep, but on the other hand there are certain indications that it does.

On an experimental basis, Neville [18] suggested that the creep rate at any time after load application is inversely proportional to the strength of the cement mortar independently of the composition of the mortar and the type of cement used. This indicates a close relationship between creep rate and gel density.

However, if a relationship exists between creep and strength as suggested by Neville, this can only be true for cement paste but not for mortar or concrete. The creep properties are highly influenced by the volume concentration of the aggregate because it immobilizes part of the total volume. The creep is actually directly proportional to the volume concentration of cement paste in concrete (T. C. Hansen [7]), whereas the strength properties are far less influenced by the amount of aggregate, as long as the water-cement ratio is kept constant.

A similar relationship, as derived earlier in this paper, between the modulus of elasticity of concrete E and the moduli of elasticity of the components E_2, E_4, and E_5 as well as the volume concentrations V_1, V_2, V_3, V_4, and V_5, can probably be established between the moduli λ_M, E_K, and λ_K describing the viscoelastic creep of concrete according to the rheological model shown in figure 5, and the moduli and volume concentrations of the components.

Analogous to eq (13) which in terms of E_M can be written:

$$\frac{1}{E_M}=\frac{V_3V_1}{V_5E_{M_5}}+\frac{V_1V_4}{E_{M_4}}+\frac{V_2}{E_{M_2}} \tag{13a}$$

we get for λ_M

$$\frac{1}{\lambda_M}=\frac{V_3V_1}{V_5\lambda_{M_5}}+\frac{V_1V_4}{\lambda_{M_4}}+\frac{V_2}{\lambda_{M_2}}. \tag{15}$$

It is assumed that the aggregate is an inert material which influences the creep only by occupying part of the volume, thus λ_{M_2} and $\lambda_{M_4} \gg \lambda_{M_5}$. (It is further assumed that V_3 does not vary much from concrete to concrete.) As a rough approximation we get eq (16):

$$\frac{1}{\lambda_M}=\frac{V_1}{V_5\lambda_{M_5}} \tag{16}$$

and analogously for E_K and λ_K

$$\frac{1}{E_K}=\frac{V_1}{V_5E_{K_5}} \tag{17}$$

$$\frac{1}{\lambda_K}=\frac{V_1}{V_5\lambda_{K_5}}. \tag{18}$$

(While eqs (16) and (17) are theoretically correct, eq (18) is only a suggested approximation.)

Grudemo [1] found, as earlier mentioned, that even large variations in the mineral composition of cement do not cause substantial changes in the microstructural composition of the cement gel. Therefore it may be assumed that the moduli of deformation of the gel component are rather constant and independent of the type and composition of cement used, and eqs (16), (17), and

(18) can be written

$$\frac{1}{\lambda_M}=\alpha\frac{V_1}{V_5} \tag{19}$$

$$\frac{1}{E_K}=\beta\frac{V_1}{V_5} \tag{20}$$

$$\frac{1}{\lambda_K}=\gamma\frac{V_1}{V_5} \tag{21}$$

where α, β, and γ=coefficients; V_1=volume concentration of cement paste in concrete; V_5=gel density. This factor is actually a function of time, $V_5(t)$.

If the rheological model shown in figure 5 is subjected to a constant stress we find

$$\frac{d\frac{\epsilon}{\sigma}}{dt}=\frac{1}{\lambda_M}+\frac{1}{\lambda_K}\exp\left(-\frac{E_K}{\lambda_K}\cdot t\right) \tag{22}$$

or integrated from the time of load application $t_1—t_1=0$ to the time $t-t_1$

$$\epsilon \text{ creep}=\frac{\epsilon_{\text{del. el.}}}{\sigma}+\frac{\epsilon_{\text{visc.}}}{\sigma}=\int_{t_1-t_1}^{t-t_1}\frac{1}{\lambda_K(t)}\exp\left(-\frac{E_{K(t)}}{\lambda_{K(t)}}\cdot t\right)dt+\int_{t_1-t_1}^{t-t_1}\frac{1}{\lambda_{M(t)}}dt \tag{23}$$

where t=age of concrete at time t, in days; t_1=age of concrete at load application, in days.

Evaluation of the First Term in Eq (23), the Delayed Elasticity

If it is assumed that the delayed elastic deformation takes place so quickly that the influence of time upon $\lambda_K(t)$ and $E_K(t)$ is the same, and small during this period, the first term in eq (23) can be written as follows:

$$\frac{\epsilon_{\text{del. el.}}}{\sigma}=\frac{1}{E_K}\left(1-e^{-m(t-t_1)}\right) \tag{24}$$

where m is a coefficient.

It was experimentally shown by L'Hermite [19] that an equation of this type very well describes the delayed elastic recovery of concrete which is actually equivalent to the pure delayed elasticity without any influence of viscosity. Thus the form of this equation is experimentally verified.

The gel density is defined according to Power's [6] (Copeland and Hayes [20] have later modified Powers' results, but this is without any importance here):

$$V_5=\frac{V_{hc}}{V_{hc}+p_c} \tag{25}$$

where V_{hc}=volume of gel, p_c=volume of capillary pores, or since

$$V_{hc}=(N+n)w_n, \text{ and } p_c=w_o-Nw_n$$

we get

$$V_5=\frac{(N+n)w_n}{n\cdot w_n+w_o}$$

where w_n=weight of nonevaporable water, in g/cc, w_o=weight of original mixing water corrected for bleeding, in g/cc, and $N=0.75(1+4k)$, where $k=0.230\ (C_3S)+0.320\ (C_2S)+0.317\ (C_3A)+0.368\ (C_4AF)$. The symbols in parentheses represent the computed weight proportions of the cement compounds indicated, and

$$n=\frac{v_c}{\frac{w_n}{C}}=\frac{v_c}{k_1}$$

where v_c=specific volume of the original cement, in cc/gram$\cong$0.31, $k_1=\frac{w_n}{C}$=weight ratio of nonevaporable water to cement when all the cement is hydrated, $k_1=0.187\ (C_3S)+0.158\ (C_2S)+0.665\ (C_3A)+0.213(C_4AF)$. Since $w_n=g(t_1)k_1\cdot C$, where $g(t_1)$=degree of hydration of cement at time t_1, C=weight of cement, in g/cc, we get from eq (25)

$$V_5=\frac{(N\cdot k_1+v_c)g(t_1)}{v_cg(t_1)+\frac{w_o}{C}} \tag{26}$$

or since $v_c\sim0.31$,

$$V_5=\frac{(N\cdot k_1+0.31)g(t_1)}{0.31g(t_1)+\frac{w_o}{C}}. \tag{27}$$

Substituting eq (27) in eqs. (19), (20), and (21) gives

$$\frac{1}{\lambda_M}=\alpha\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)} \tag{28}$$

$$\frac{1}{E_K}=\beta\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)} \tag{29}$$

$$\frac{1}{\lambda_K}=\gamma\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}. \tag{30}$$

Substituting eq (29) in eq (24) gives

$$\frac{\epsilon_{\text{del. el.}}}{\sigma}=\beta\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}\left(1-e^{-m(t-t_1)}\right). \tag{31}$$

Evaluation of the Second Term in Eq (23), the Viscosity

Substituting eq (28) in the viscosity term of eq (23) gives

$$\frac{\epsilon_{\text{visc.}}}{\sigma}=\int_{t_1}^{t}\frac{1}{\lambda_M(t)}\,dt=\int_{t_1}^{t}\alpha\,\frac{\left(0.31g(t)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t)}\,dt \tag{32}$$

or possibly

$$\frac{\epsilon_{\text{visc.}}}{\sigma}=\int_{t_1}^{t}\alpha(t)\,\frac{\left(0.31g(t)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t)}\,dt. \tag{32a}$$

Not knowing the functions $g(t)$ and $\alpha(t)$ with any accuracy is a serious obstacle against an integration of eq (32a). It is known, however, that the creep curves obtained when creep is plotted against the logarithm of time are approximately straight lines at later stages when all the delayed elastic deformation has taken place (see Hanson [21], Bäckström [22], and Serafim and Guerreiro [23]. Moreover, the curves obtained when creep is plotted against time are parallel at later stages for concretes made at the same time but loaded at different ages (see, e.g., Glanville [24], McHenry [25], and Bäckström [22]). Therefore such creep curves must also be parallel at later stages in a semilogarithmic graph. Consequently, it is to be expected that the viscous part of creep can be approximated by the following function of time:

$$\frac{\epsilon_{\text{visc.}}}{\sigma}=\text{const}\cdot\ln\frac{t}{t_1} \tag{33}$$

where t=age of concrete at time t, in days; t_1=age of concrete when loaded, in days.

Considering the influence of composition of concrete, it is suggested that eq (32) or (32a) can be written as

$$\frac{\epsilon_{\text{visc.}}}{\sigma}=\alpha_1\frac{w_o}{C}V_1\ln\frac{t}{t_1}. \tag{34}$$

It must be remarked that the linearity between specific creep (i.e., creep per unit stress) and time in a semilogarithmic graph is only valid up to about 1,000 days sustained loading of a young concrete. (Davis and Troxell [26].) Thereafter the creep rate is considerably reduced probably due to recrystallization in the cement gel, and the creep obtained after another 20 yr sustained loading is only slightly greater than the creep obtained after 1,000 days sustained loading.

Substituting eq (31) and eq (34) in eq (23) gives *the general rheological creep equation of all cement pastes, mortars, and concretes when cured and stored in water (or under other conditions where no drying or wetting can take place) and subjected to a constant compressive, tensile, or flexural load.*

$$\underset{\substack{\text{(Creep per}\\\text{unit stress)}}}{\frac{\epsilon_{\text{creep}}}{\sigma}}=\underset{\text{(Delayed elasticity)}}{\beta\,\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}\left(1-e^{-m(t-t_1)}\right)}+\underset{\text{(Viscosity)}}{\alpha_1\frac{w_o}{C}\cdot V_1\ln\left(\frac{t}{t_1}\right)} \tag{35}$$

where t=age of concrete at time t, in days, t_1=age of concrete when loaded, in days, w_o/C=water-cement ratio by weight, corrected for bleeding, V_1=volume concentration of cement paste in mortar or concrete, $g(t_1)$=degree of hydration of cement at the time of load application, α_1, β, and m=coefficients to be determined experimentally, k_1=weight ratio of nonevaporable water to cement when all cement is hydrated. k_1 is a function of the proportions of cement components: k_1=0.187 (C_3S)+0.158 (C_2S)+0.665 (C_3A)+0.213 (C_4AF). N=0.75 (1+4k), where k=0.230 (C_3S)−0.320 (C_2S)+0.317 (C_3A)+0.368 (C_4AF).

The strain response of any stress, or the stress response of any strain, constant or varying, and applied at any time to any concrete, can be predicted from a similar analysis of the rheological model shown in figure 5. Due consideration should be paid to our present knowledge of the physical structure and properties of concrete. It must, however, be remembered that this model is only valid for normal working stresses under the plastic limit where no internal microcracking occurs (see T. C. Hansen [7] and [27]), and that the model does not take into account the phenomenon of permanent set.

Experimental Verification

All creep tests found in the literature which meet with the following two requirements are grouped in table 3.

1. Test specimens have been loaded in water after continuous storage in water. This provides us with results on basic creep under very well-defined conditions.
2. Test specimens have been loaded under the proportional or plastic limit where no microcracking has occurred, which, where no other information is available, is estimated to be at least 30–40 percent of the short-time strength.

The 42 creep tests listed, provide us with good material for experimental verification of eq (35).

In estimating the values of the parameters in eq (35) for all these creep tests, the following approximations have been made.

When the composition of the cement used is unknown, and therefore it has not been possible to calculate k and k_1, it has been assumed according to Powers and Brownyard [4] that k=0.25 and k_1=0.23.

Further it has been assumed according to Hummel [28] that the two curves a and b in figure 6

Table 3. *Concrete data for comparison between calculated and experimentally determined creep values*

No.	Ser.	Type of test	Age at load application days	$g(t_1)$ degree of hydration at load application	$\frac{w}{c}$, $\frac{w_o}{C}$ by weight	V_1, vol. concentration of cement paste	Type of cement	k	k_1	N	$\frac{\epsilon}{\sigma}$ Specific creep after 50 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 100 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 200 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 900 days sustained loading		Notes
											Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	
1 Davis [29]	2	Compr.	2	0.2	0.64	0.330	Normal	0.25	0.23	1.50	8.35	10.00	9.99	11.50	10.93	12.50	12.71	13.70	
2 Davis [30]	2	do	7	.4	.64	.330	do	.25	.23	1.50	4.93	6.16	6.13	6.44	7.01	7.20	8.79	7.85	
3 do	2	do	7	.4	.64	.330	do	.25	.23	1.50	------	------	------	------	------	------	------	------	Loaded over plastic limit.
4 do	2	do	28	.7	.64	.330	do	.25	.23	1.50	2.78	2.88	3.64	4.00	4.39	5.05	6.09	5.70	
5 do	2	do	28	.7	.64	.330	do	.25	.23	1.50	------	------	------	------	------	------	------	------	Loaded over plastic limit.
6 do	2	do	28	.7	.64	.330	do	.25	.23	1.50	------	------	------	------	------	------	------	------	Loaded over plastic limit.
7 do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.02	2.44	2.50	2.98	3.10	4.44	4.30	
8 do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.34	2.44	2.78	2.98	3.50	4.44	5.15	
9 do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.96	2.44	3.33	2.98	3.92	4.44	5.25	
10 Davis [31]	Reinf. test.	do	28	.7	.76	.250	do	.25	.23	1.50	2.45	2.63	3.21	3.46	3.91	5.10	------	------	
11 do	Reinf. test.	do	28	.7	.49	.305	do	.25	.23	1.50	2.03	1.96	2.68	2.73	3.24	3.65	------	------	
12 do	3	do	28	.7	.55	.286	do	.25	.23	1.50	2.13	3.24	2.78	3.57	3.35	3.95	------	------	
13 Davis [30]	7	do	28	.7	.44	.330	do	.25	.23	1.50	2.04	2.08	2.65	2.50	3.19	3.50	------	------	
14 do	7	do	28	.7	.61	.255	do	.25	.23	1.50	2.07	2.53	2.72	2.82	3.28	3.20	------	------	
15 Davis [31]	14	do	90	.9	.57	.250	do	.25	.23	1.50	1.27	2.14	1.70	2.30	------	------	------	------	
16 do	16	do	28	.7	.71	.290	do	.25	.23	1.50	2.68	3.65	3.43	4.20	------	------	------	------	
17 Dutron [32]	PP350	do	60	.9	.69	.305	H.E. Str.	.25	.23	1.50	1.98	2.15	2.67	2.55	3.29	3.95	4.85	6.30	
18 do	PP350	do	60	.9	.69	.305	do	.25	.23	1.50	1.98	1.61	2.67	2.30	3.29	3.20	4.85	5.05	
19 do	PP350	do	60	.9	.69	.305	do	.25	.23	1.50	1.98	1.41	2.67	2.15	3.29	2.85	4.85	4.70	
20 do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	1.32	1.82	1.64	2.12	2.65	3.10	3.70	
21 do	GR300	do	60	.9	.56	.234	do	.25	23	1.50	1.33	1.26	1.82	1.58	2.12	2.35	3.10	2.75	
22 do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	.90	1.82	1.40	2.12	1.96	3.10	2.40	
23 do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	.88	1.82	1.30	2.12	1.83	3.10	2.45	
24 do	PP350	do	14	.7	.69	.305	do	.25	.23	1.50	3.32	2.20	4.32	3.72	5.11	5.13	6.85	7.22	
25 do	PP350	do	14	.7	.69	.305	do	.25	.23	1.50	3.32	2.15	4.32	3.32	5.11	4.66	6.85	5.90	
26 Bergstrom [33]	PH	Flex.	28	.7	.35	1.000	Normal	.23	.20	1.44	5.42	5.72	7.04	7.20	------	------	------	------	
27 do	PJ	do	28	.7	.25	1.000	do	.23	.20	1.44	4.22	4.15	5.44	5.36	------	------	------	------	
28 do	PM	do	28	.7	.30	1.000	do	.23	.20	1.44	4.81	5.25	6.24	7.15	------	------	------	------	
29 do	PN	do	28	.7	.30	.800	do	.23	.20	1.44	3.84	6.25	4.99	7.56	------	------	------	------	
30 Hansen (unpubl)	B	do	28	.7	.37	.590	do	.23	.20	1.44	3.32	3.71	4.33	4.83	------	------	------	------	
31 Neville [18]	Cem 1	Compr.	28	.7	.40	.377	do	.25	.24	1.50	2.06	2.95	2.69	3.50	------	------	------	------	$\frac{\epsilon}{\sigma}$ Meas. is corrected for shrinkage according to the capacity of creep.
32 do	do 2	do	28	.7	.40	.377	do	.25	.23	1.50	2.10	2.95	2.75	3.50	------	------	------	------	
33 do	do 3	do	28	.7	.40	.377	do	.25	.23	1.50	2.10	2.06	2.75	2.30	------	------	------	------	
34 do	do 4	do	28	.7	.40	.377	Sulph. res.	.26	.18	1.53	2.31	2.26	3.00	2.50	------	------	------	------	
35 do	do 5	do	28	.7	.40	.377	Normal	.25	.23	1.50	2.10	3.10	2.75	3.30	------	------	------	------	
36 do	do 6	do	28	.7	.40	.377	do	.26	.22	1.53	2.15	2.85	2.80	3.10	------	------	------	------	
37 do	do 7	do	28	.7	.40	.377	do	.26	.22	1.53	2.15	2.25	2.80	2.40	------	------	------	------	
38 do	do 8	do	28	.7	.40	.377	White	.24	.21	1.47	2.25	2.66	2.92	2.90	------	------	------	------	
39 do	do 9	do	28	.8	.40	.377	H.E. Str.	.24	.23	1.47	2.04	2.15	2.70	2.30	------	------	------	------	
40 do	do 10	do	28	.7	.40	.377	Low heat	.27	.18	1.56	2.27	2.85	3.17	2.90	------	------	------	------	
41 do	do 11	do	28	.7	.40	.377	Sulph. res.	.28	.19	1.59	2.28	2.30	2.97	2.30	------	------	------	------	
42 Serafim [23]	Stage 2	Saturated compr.	8	.45	.50	.257	Normal	.25	.23	1.50	2.84	3.40	3.55	4.0	------	------	------	------	

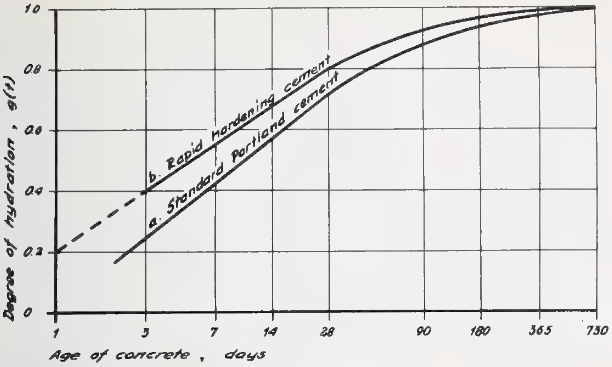

FIGURE 6. *Graph showing degree of hydration versus age of concrete.*
(Hummel [26].)

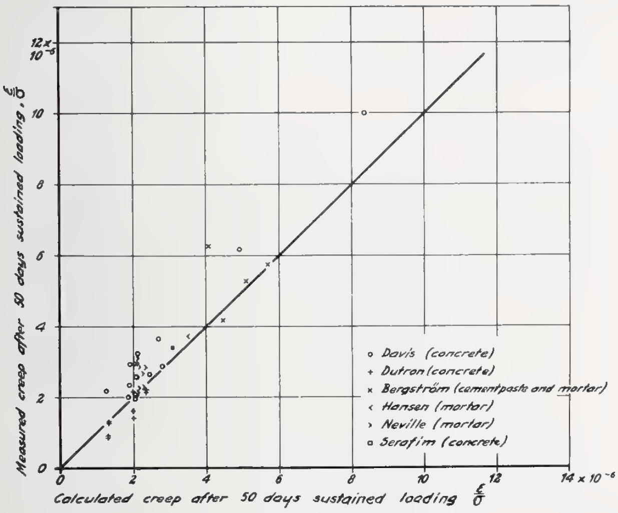

FIGURE 7. *Graph showing agreement between calculated and experimentally determined creep after 50 days sustained loading.*

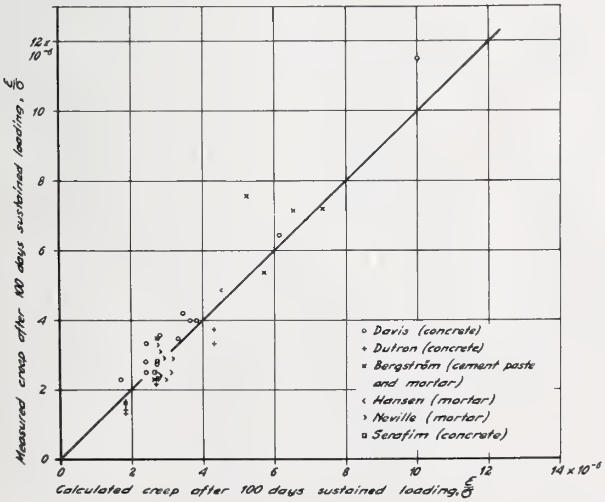

FIGURE 8. *Graph showing agreement between calculated and experimentally determined creep after 100 days sustained loading.*

give the increase in strength or in degree of hydration with time for average standard portland cement, and for rapid hardening cement.

Figures 7–10 show agreement between experimentally determined creep values after 50, 100, 200, and 900 days sustained loading, and creep values calculated from eq (35). (The full line curves correspond to the ideal case where the computed creep values are equal to the experimentally determined values.) The coefficients are

$$\beta = 3.06 \cdot 10^{-6}$$

$$m = 0.0333$$

$$\alpha_1 = 5.7 \cdot 10^{-6}.$$

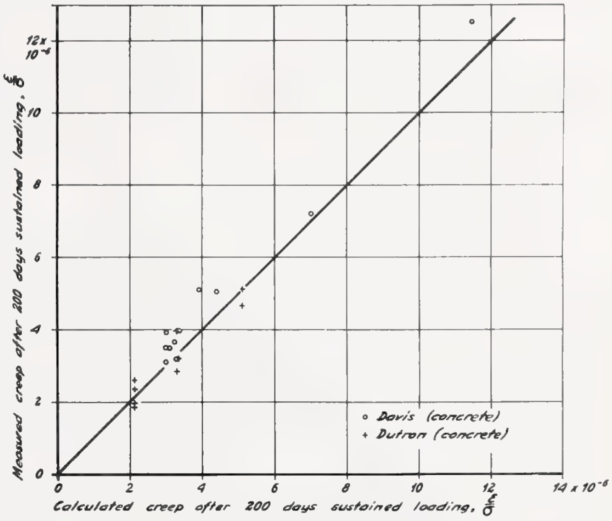

FIGURE 9. *Graph showing agreement between calculated and experimentally determined creep after 200 days sustained loading.*

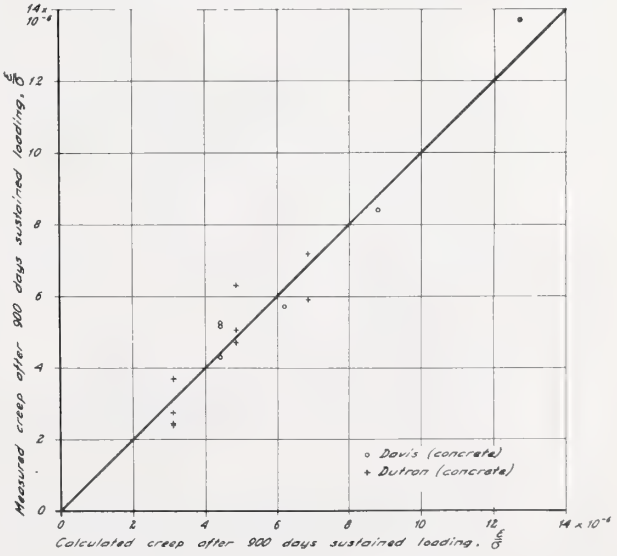

FIGURE 10. *Graph showing agreement between calculated and experimentally determined creep after 900 days sustained loading.*

Using these values, *the fundamental equation for creep of water-stored concrete, mortar, and cement paste can be written as follows:*

$$\frac{\epsilon_{\text{creep}}}{\sigma}=3.06\cdot 10^{-6}\frac{\left(0.31g(t_1)+\frac{w_o}{C}V_1\right)}{(Nk_1+0.31)g(t_1)}(1-e^{-0.0333(t-t_1)})$$
$$+5.7\cdot 10^{-6}\frac{w_o}{C}V_1\ln\left(\frac{t}{t_1}\right) \quad (35a)$$

where all symbols are defined as in eq (35).

It is remarked that the experimental creep values in table 3 include flexural and compressive creep tests on concrete, mortar, and cement paste made from different cements and different aggregate material in different laboratories all over the world in the years 1930–1958. Considering this fact and the large scatter found even in very well-controlled creep tests, the average percentage deviations of 12–16 percent between measured and calculated creep values in table 3 are not surprising.

The rather large deviations between our calculated creep values and some of Neville's experimental data on creep of mortars of the same composition but made with different cements indicate that part of the uncertainty in the calculated values can be explained by the fact that the degree of hydration of the different cements cannot be estimated accurately enough from the two average curves a and b in figure 6.

Appendix 1

List of Repeatedly Used Symbols

a = constant

α = constant

α_1 = constant

b = coefficient

β = coefficient

C = weight of cement, in grams per cc of paste

c = coefficient

d = coefficient

δ = proportionality factor between V_m and total volume of gel V_{hc}

$E_M=E$ = modulus of elasticity of concrete, kg/cm²

$E_{M_1}=E_1$ = modulus of elasticity of cement paste or mortar, kg/cm²

$E_{M_2}=E_2$ = modulus of elasticity of aggregates, kg/cm²

$E_{M_3}=E_3$ = modulus of elasticity of gel and pores in cement paste, kg/cm²

$E_{M_4}=E_4$ = modulus of elasticity of unhydrated cement grains in cement paste, kg/cm²

$E_{M_5}=E_5$ = modulus of elasticity of cement gel, kg/cm²

$E_{M_6}=E_6$ = modulus of elasticity of capillary pores = 0

$E_{K_{1\text{to}6}}$ = modulus of delayed elasticity (see fig. 5) of the respective components, kg/cm²

E_s = modulus of elasticity for a soft component of a combined material, kg/cm²

E_h = modulus of elasticity for a hard component of a combined material, kg/cm²

e = base of natural or Napierian logarithms

ϵ = elastic strain of a combined material

ϵ_s = strain of the soft component of a combined material

ϵ_h = strain of the hard component of a combined material

ϵ_{creep} = creep strain

$\epsilon_{\text{del. el.}}$ = delayed elastic strain

$\epsilon_{\text{visc.}}$ = viscous strain

F_c = strength of cement paste, mortar or concrete, kg/cm²

$g(t_1)$ = degree of hydration of cement at age t_1 when concrete is loaded

γ = coefficient

k = constant, characteristic of the cement, related to the computed compound composition as follows: $k=0.230\ (C_3S)+0.320\ (C_2S)+0.317\ (C_3A)+0.368(C_4AF)$

$k_1=\frac{w_n}{C}$ = weight ratio of nonevaporable water to cement where all the cement is hydrated; k_1 is related to the computed compound composition of the cement as follows: $k_1=0.187(C_3S)+0.158(C_2S)+0.665(C_3A)+0.213(C_4AF)$

$\lambda_{M_{1\text{to}6}}$ = Troutons coefficient of viscous traction for Maxwell element (see fig. 5) of respective components, kg sec/cm²

$\lambda_{K_{1\text{to}6}}$ = Troutons coefficient of viscous traction for Kelvin element (see fig. 5) of respective components, kg sec/cm²

m = coefficient

N = $0.75(1+4k)$

p_c = volume of capillary pores, in cc/cc of cement paste

σ = stress, kg/cm²

σ_s = stress on the soft component of a combined material, kg/cm²

σ_h = stress on the hard component of a combined material, kg/cm²

t = age of concrete, days

t_1 = age of concrete when loaded, days

V_s = volume concentration of the soft component of a combined material

V_h = volume concentration of the hard component of a combined material

V_{hc} = volume of hydrated cement = volume of gel, cc/cc of cement paste

V_m = constant, proportional to the surface area of the gel; theoretically the number of grams of water required to cover the surface of the hydrated cement in 1 cc of cement paste with a layer averaging one molecule deep

V_1 = volume concentration of cement paste in concrete

V_2 = volume concentration of aggregate in concrete

V_3 = volume concentration of gel and capillary pores in cement paste

V_4 = volume concentration of unhydrated cement grains in cement paste

$V_5=\frac{V_{hc}}{V_{hc}+p_c}$ = volume concentration of gel in the component of cement paste which consists of gel and pores = gel density

V_6 = volume concentration of pores in the component of cement paste which consists of gel and pores

v_c = specific volume of the original cement, cc/gram $\cong 0.31$

w_o = weight of original water content corrected for bleeding, g/cc of cement paste

w_n = weight of nonevaporable water, g/cc of cement paste

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Paper V–S3. A Few Unsolved Problems of Cement Hydration*

Wolfgang Czernin

Synopsis

The writer deals with some problems of cement hydration which have been mentioned in the papers and discussions of this Symposium.

The "Dormant Period". Although some facts seem to indicate that there exists a "dormant period" after the mixing of cement with water, the writer—on the basis of his own experiments and those of others—believes that the stiffening of cement pastes starts immediately after mixing. The stiffening phenomena can, however, be obscured in tests where the thixotropic properties or the "memory" of the paste can play their part.

Does Hydration Proceed by Solution and Precipitation or by Topochemical Reaction? The writer produces electronmicrographs obtained by use of carbon replicas of hydrating C_3S which seems to show that topochemical hydration reactions are accompanied by solution and precipitation reactions which lead to deposits in the capillary spaces. Thus it is indicated that both kinds of reaction take place during the hydration of cement.

The Constancy of Cement Gel Porosity. The assumption of a constant porosity of the cement gel independent of the water cement factor does not seem to be in accordance with Abrams' law: If the porosity of the hydrated parts remains the same, whatever the amount of unhydrated material distributed in the gel, then strength should remain at the same level or at least near it when we lower the w/c from 0.4 to the lowest possible ratio. This, however, is, as we all know, not the case.

Résumé

L'auteur traite certains problèmes de l'hydratation du ciment qui ont été mentionnés dans les exposés et discussions de ce Symposium.

La "Période dormante". Bien que certains faits semblent indiquer qu'il existe une "période dormante" après le mélange du ciment avec l'eau, l'auteur —s'appuyant sur ses propres expériences et sur d'autres— croit que le durcissement des pâtes de ciment commence immédiatement après le mélange. Cependant les phénomènes de durcissement peuvent être cachés dans les expériences où les propriétés thixotropiques ou la "mémoire" de la pâte peuvent jouer un rôle.

Est-ce que l'Hydratation procède par Solution et Précipitation ou par Réaction Topochimique? L'auteur présente des électronmicrographes obtenus au moyen de répliques au carbone de l'hydratation de C_3S qui semblent indiquer que les réactions topochimiques d'hydratation s'accompagnent de réactions de solution et de précipitation qui mènent à des dépôts dans les espaces capillaires. Ainsi il est indiqué que les deux sortes de réactions ont lieu pendant l'hydratation du ciment.

Constance de la Porosité du Gel de Ciment. L'hypothèse d'une porosité constante du gel de ciment indépendante du facteur de l'eau dans le ciment ne paraît pas conforme à la loi d'Abrams: Si la porosité des parties hydratées reste la même, quelle que soit la quantité de matière nonhydratée distribuée dans le gel, la résistance devrait rester au même niveau ou du moins très proche quand nous diminuons le e/c de 0.4 au rapport le plus bas possible. Ceci cependant, et nous le savons tous, n'est pas le cas.

Zusammenfassung

Der Autor beschäftigte sich mit einigen Problemen der Zementhydratation, die auch von anderen Forschern, die in diesem Symposium berichtet haben, untersucht worden sind.

"Dormant Period." Man kann aus einigen Beobachtungen schließen, daß nach dem Mischen des Zements mit Wasser eine Latenzzeit vorhanden ist, aber der Autor glaubt unter Bezugnahme seiner eigenen Arbeiten und die Ergebnisse anderer Forscher, daß Zementpasten doch sofort nach dem Anmachen zu härten beginnen. Dieses Härten kann in Fällen, in welchen sich die thixotropischen Eigenschaften oder das "Gedächtnis" der Mischung bemerkbar machen, häufig nicht durch Messungen veranschaulicht werden.

Wird die Hydratation durch ein Auflösen und Ausfallen, oder durch eine topochemische Reaktion hervorgebracht? Der Autor zeigte einige Elektronmikrographien, die er durch Kohlehüllenbilder des hydratisierenden C_3S erhielt, aus denen ersichtlich ist, daß Hydratationsreaktionen an der Oberfläche von Auflösungen und Ausfällungen die zu Ablagerungen im Kapillarraum führen, begleitet sind. Das heißt also, daß beide Reaktionsarten treten während der Zementhydratation auf.

Die Unveränderlichkeit der Porosität des Zementgels. Man hat angenommen, daß die Porosität eines Zementgels konstant ist und nicht vom Wasser-Zementfaktor abhängt; aber das scheint im Widerspruch zum Gesetz von Abrams zu sein. Wenn man nämlich annimmt, daß die Porosität der hydratisierten Anteile sich nicht ändert, ganz egal der Menge des unhydratisierten Materials das in dem Gel verteilt ist, dann sollte auch die Festigkeit unverändert bleiben, oder doch wenigstens ungefähr so, wenn das Verhältnis Wasser / Zement von 0,4 bis zum kleinstmöglichsten Wert erniedrigt wird. Aber, wie es ganz allgemein bekannt ist, das ist garnicht der Fall.

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[*] Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Verein der Österreichischen Zementfabrikanten, Vienna, Austria.

Introduction

Although the papers on the hydration of cement as presented at this Symposium demonstrate in an impressive way the progress in the past decade of our knowledge of the behavior of cement, there still are many questions open to discussion which will have to be answered before we can say that we really understand cement.

Among these the writer wants to deal with the following items:

The "dormant period".

Solution-precipitation vs. solid-state hydration.

The constancy of cement gel porosity.

The "Dormant Period"

Discussing "Early Hydration Reactions," K. T. Greene [1][1] points out the conflicting facts that though the bleeding rate of cement pastes has been found to be remarkably constant for a considerable time, thus indicating a "dormant period" in the process of hydration, results of mechanical tests have been reported which seem to point to the contrary. These results indicating progressive stiffening of the pastes have, however, in their turn been contradicted by others showing that the paste does not change its physical characteristics to an appreciable degree for the first hour or so after mixing.

The writer's own experiments are in accordance with those of Dorsch [2], Humm [3] and Francardi [4]: Stiffening of cement pastes seems to begin immediately after mixing. Figure 1 shows the equipment used by the writer for his tests.

The cement paste is put on a balance in a Vicat-ring. A needle (3 mm in diameter) is then driven into the paste at a constant speed (10 cm/min) by means of a motor. The stiffer the mix, the more the balance will be deflected so that the resistance to the penetration of the needle can be read directly from the scale. Figure 2 shows a few test results obtained with two different cements. The tests started immediately after mixing, placing, and de-airing the paste, i.e., 7 min after the addition of water to the cement.

This kind of test is rather sensitive and shows among other things the surprising "memory" of pastes of normal consistency The penetration of the needle even into a fresh paste will cause a displacement of solid matter which seems to a considerable degree to be irreversible. Even after a long lapse of time the repenetrating needle does not find appreciable resistance.

Keil [5] and Kozlowski [6] as well as Greene [1] himself did not in their experiments find significant thickening up to 2 hr or so. But as Greene points out, his pastes were continuously agitated, while Keil agitated his prior to the consistency measurements. Kozlowski, while not actually agitating his sample, used a single paste specimen for measuring consistency at regular intervals with a penetration rod.

This writer believes that the stiffening of cement pastes starts immediately after mixing. This phenomenon however can be concealed in tests where the thixotropic properties or the "memory" of the paste can play their part.

It is therefore felt that the "constant bleeding rate" must find another explanation than that of a "dormant period"

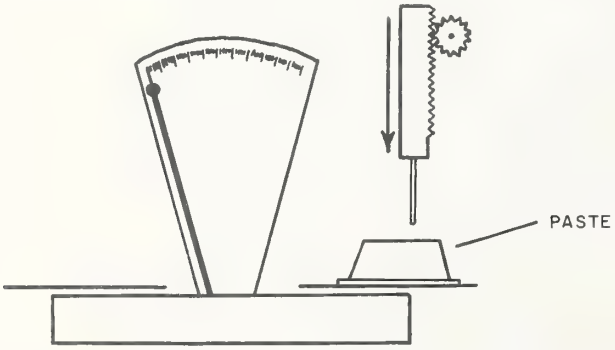

FIGURE 1. *Device for measuring the stiffening of cement paste at early ages.*

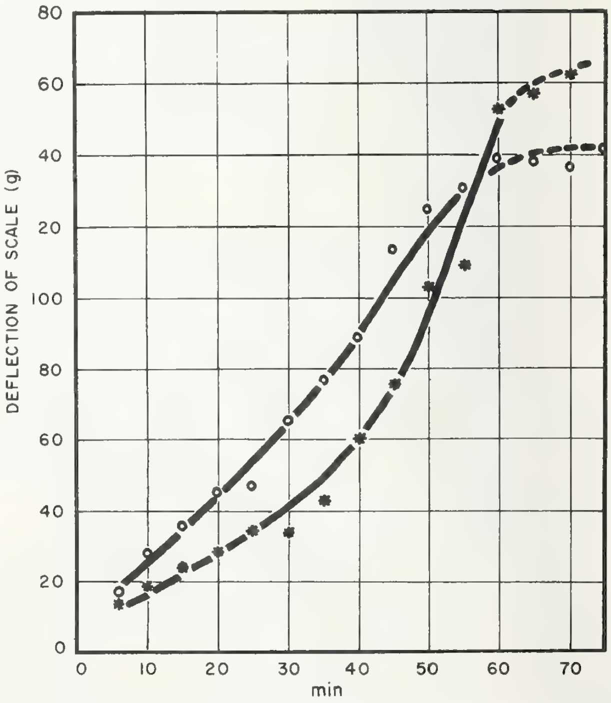

FIGURE 2. *Resistance to penetration of two portland-cement pastes of standard consistency at early ages.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

Does Hydration Proceed by Solution and Precipitation or by Topochemical Reaction?

The accompanying electronmicrographs [2]—though published previously by the writer [7]—are presented here because they seem to show that topochemical reactions do not play an important part in cement hydration. The cement grains in figure 4, from 6 to 9 μ in diameter, have been obtained by sedimentation of a laboratory-made "alite" cement of the following composition: C_3S, 90 percent; C_2S, 1 percent; C_3A, 2.7 percent; C_4AF, 1.3 percent; free CaO, 1.4 percent. There was no need to add any gypsum as the cement was slow setting.

A paste corresponding to a w/c ratio of 0.6 was prepared with this cement and spread thinly on a microscope slide. The well-wetted grains then could be imagined standing in a "foot bath" as sketched in figure 3. When, immediately after the spreading of the paste, the slide was put in a desiccator over $CaCl_2$ it dried very quickly and cannot have been in contact with evaporable water for more than 5 min. This state of hydration is shown in figure 4. Though the reaction time was short, the film of evaporated water left a residue of well-developed hexagonal crystals, and on the grain surface left products of a topochemical reaction. If the paste is preserved in moist air for 1 hr, the picture—figure 5—looks different. The grains are covered by a growth of rolled and wrinkled foils, as can more distinctly be seen in the higher magnification in figure 6. But these foils can also be found in what might be called the capillary space. This deposit in the capillary space is much more strongly pronounced after 24 hr of moist curing (fig. 7). It seems difficult to imagine that such a deposit could have been produced in the capillary space if hydration had proceeded as a solid-liquid reaction. Figure 8, finally, shows the state of things after 28 days of moist curing. The darker and more uniform parts correspond to the original cement grains. Seen through a stereoscope they sharply protrude out of what was formerly the capillary space.

These pictures may not yet give an unequivocal answer to the questions at hand. But it is believed that we have here a technique which might be helpful in the future in solving this and other problems of cement hydration. (Notice for instance the remarkable change in the aspect of the cement grains during the first hour; surely this does not look like a "dormant period".) This writer is fully aware that identification of paste constituents must for the time being remain one of the main objectives of electron microscopy in this field of research. Grudemo's excellent paper on the "Microstructure of Hardened Paste" presented at this Symposium [8] is an outstanding example of that kind of work. Contrary to Grudemo's view, however, this writer believes that replica methods when handled with skill and experience can resolve the finest details of the paste surface.[3] This fact, together with the enormous depth of focus of the electron microscope which allows the most revealing stereoscopic observations, seem to be advantages of the replica technique well worth while following up in the study of cement hydration.

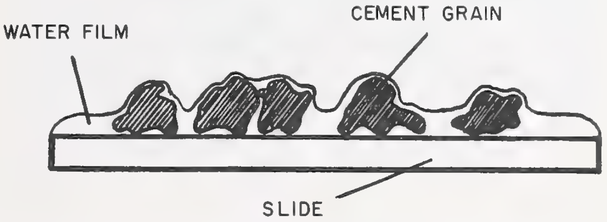

Figure 3. *Schematic drawing of portland-cement paste on microscope slide.*

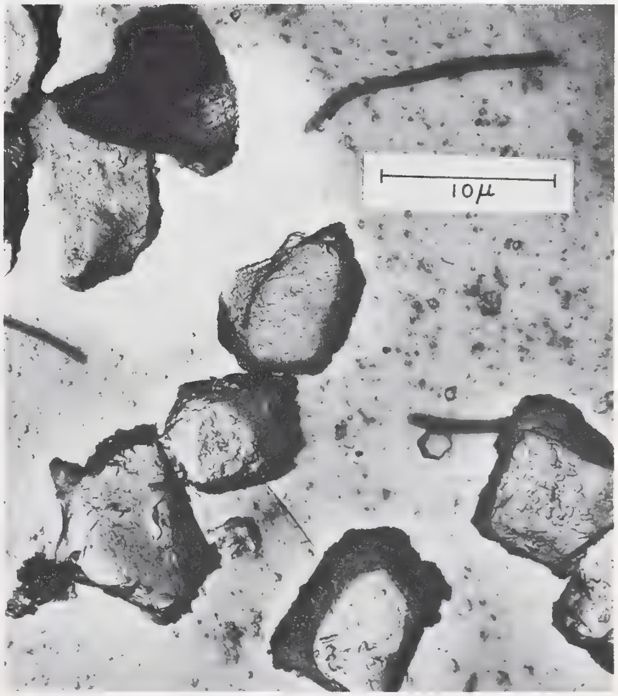

Figure 4. *Cement paste hydrated 5 min.*

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[2] The electronmicrographs have been obtained by use of carbon replicas in collaboration with F. Grasenick, director of the Electronmicroscopic Institute of the Technical University, Graz, Austria.

[3] See Grasenick's stereophotos of carbon replicas of periclase crystals, Zement u. Beton, No. 16 (July 1959), page 18.

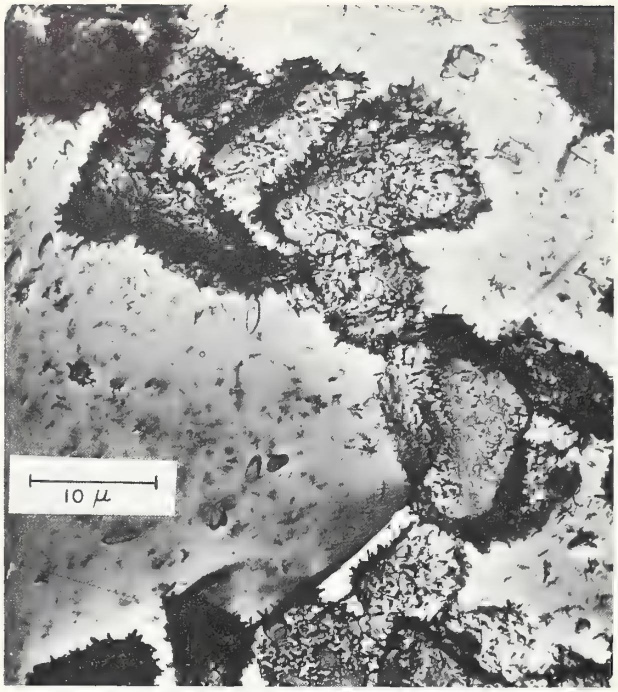

FIGURE 5. *Cement paste hydrated 1 hr.*

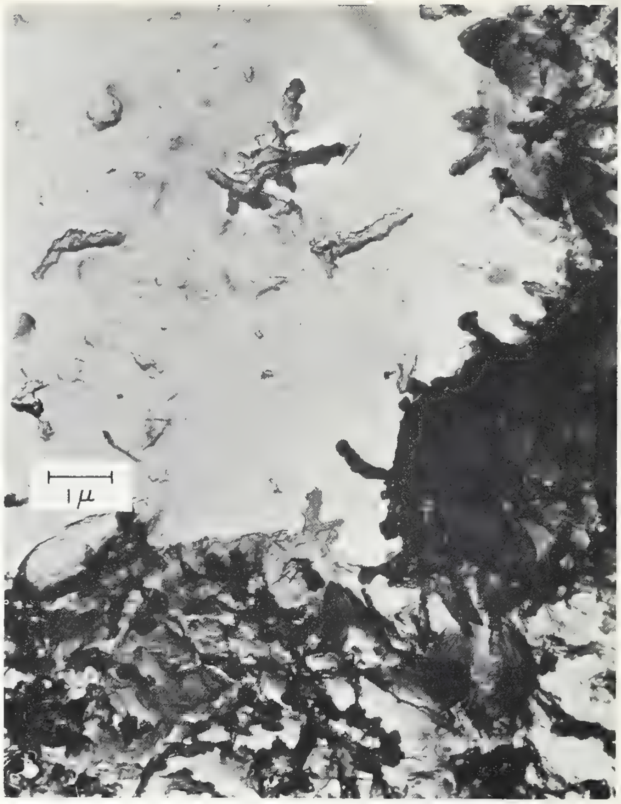

FIGURE 7. *Cement paste hydrated 24 hr (high magnification).*

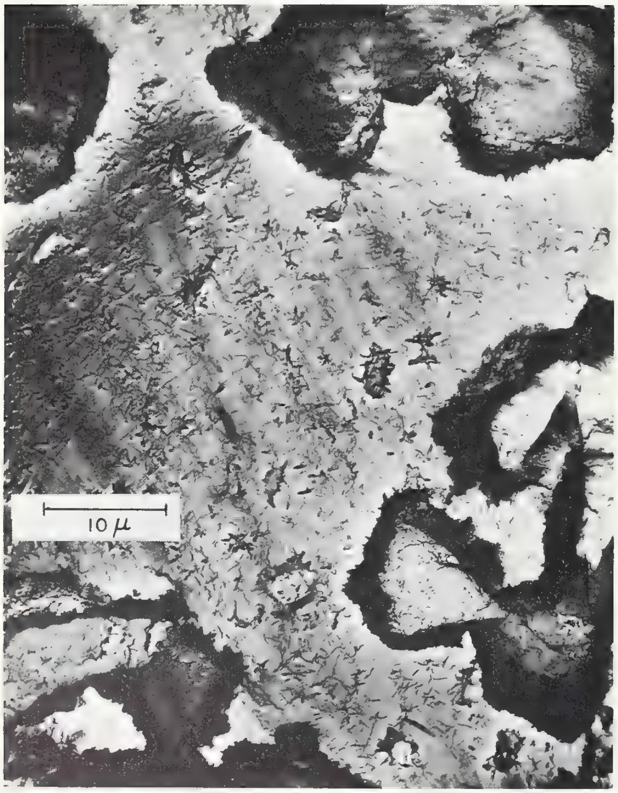

FIGURE 6. *Cement paste hydrated 24 hr.*

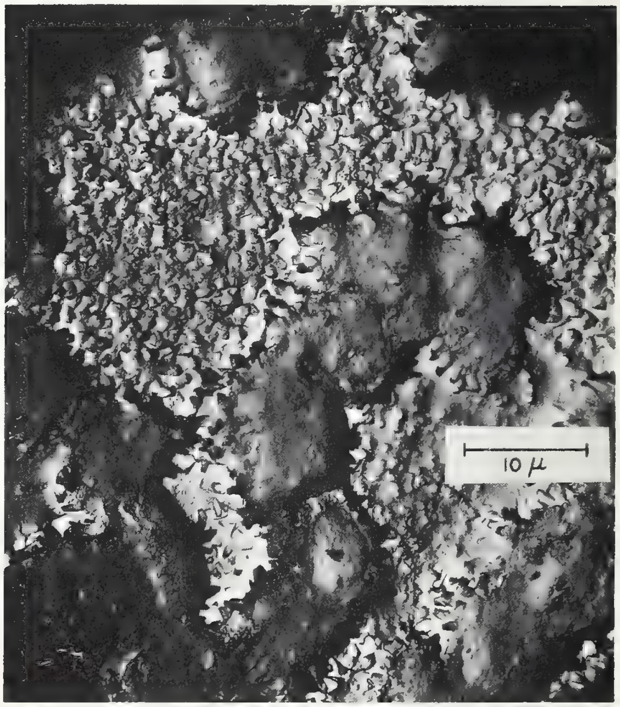

FIGURE 8. *Cement paste hydrated 28 days.*

The Constancy of Cement Gel Porosity

In his paper "On the Physical Properties of Cement Paste" presented at this Symposium [9], T. C. Powers states that "when the cement content is at the limit for complete hydration the porosity of a completely hydrated specimen is at a minimum. At any higher cement content the porosity of the paste is lower only because of the presence of unhydrated cement; the porosity of the hydrated part remains the same." This means, inter alia, that the water in the gel pores, though evaporable and able to migrate, is unable to react with unhydrated cement. Powers, while raising the question whether stoppage of hydration is virtual or real, discusses a few of the present writer's experiments, which attempted to force the hydration of cement samples with water added in quantities not sufficient for the full hydration of the cement. This forced hydration was attempted through continued ball-milling of the mixture. By this procedure, however, the evaporable water could not be reduced below a certain level corresponding to a gel porosity of ~21 percent. Thus Powers' finding seemed to be confirmed qualitatively, but not quantitatively, as the minimum porosity found in the Portland Cement Association laboratories did not fall below 28 percent.

In trying to explain this divergence Powers reasons that self-desiccation as it happens in the ball mill must lead to a lesser amount of evaporable water than is present in a corresponding water-cured sample. While in the sealed container some capillary space will become empty through self-desiccation, that space will be filled with additional water in the case of the water-cured specimen. But in the opinion of the present writer this additional water will not remain capillary water but will react in its turn with unhydrated cement as long as capillary space is available. Thus it seems as if we could expect the same w_n/w_e values in both cases.

Even if this reasoning should be correct, the ball-mill experiment is of course not conclusive with respect to the validity of Powers' theory of constant gel porosity.

There is another point, however, which seems incompatible with the conception of a constant gel porosity. If the porosity of the hydrated parts remains the same, whatever the amount of unhydrated material distributed in the gel, then the strength should remain at the same level or at least near it when we lower the w/c ratio from 0.4 to the lowest possible ratio. But we know that the strength curve proceeds without a break as a straight line towards fabulous figures in accordance with Abram's law.

The writer is aware that his discussion of certain unsolved problems has not contributed much to their solution. He hopes nevertheless to have drawn the attention to a few points where further work seems needed.

References

[1] K. T. Greene, this Symposium, Paper IV–1.
[2] K. E. Dorsch, Cement and Cement Manuf. **6,** 45–53 (1933).
[3] W. Humm, Zement-Kalk-Gips **3,** 118–120 (1950).
[4] M. T. Francardi, Compte rendue du XXXI Congrès Internationale de Chimie Industrielle, Liège, Septembre 1958.
[5] F. Keil, Zement **28,** 729 (1939).
[6] C. Kozlowski, Zement u. Beton, No. 16, Vienna, Austria (1959).
[7] W. Czernin, Betonsteinzeitung **25,** 376–382 (1959).
[8] A. Grudemo, this Symposium, Paper V–2.
[9] T. C. Powers, this Symposium, Paper V–1.

Paper V–S4. The Rheology of Fresh Portland Cement Pastes*

Moshe Ish-Shalom and S. A. Greenberg

Synopsis

The flow behaviors of fresh pastes were examined in order to obtain information on these properties and to try to correlate the properties with the physicochemical nature of the pastes. Rheological measurements were performed with a coaxial cylinder viscometer. With this instrument rpm-torque plots were determined as a function of several variables. Plots were made with increasing rpm (upcurve) and decreasing rpm (downcurve) as a function of torque. From these plots parameters related to yield values, f, and plastic viscosities, U, were evaluated. Among the variables studied were: (1) chemical compositions of cements, (2) mixing conditions, (3) surface areas of cements, and (4) temperature of hydration.

The data showed that three types of rheological behavior are frequently found in pastes: (1) antithixotropic, (2) reversible, and (3) thixotropic. Antithixotropic behavior was detected in pastes which had been vigorously agitated and were allowed to hydrate to a small extent. Antithixotropic behavior is characterized by a flow curve (rpm-torque) in which the descending portion (decreasing rpm) is to the *right* of the upcurve (increasing rpm). The reversible rpm-torque flow curves were exhibited by pastes which were allowed to hydrate for about 45 min. The predominant kind of flow curve was thixotropic. The pastes are essentially thixotropic in flow behavior, with the other types mainly deviations from this behavior. Thixotropy is characterized by a flow curve in which the descending branch is to the *left* of the upcurve.

It is proposed that thixotropy is characteristic of the hydrogel formed by hydration of the calcium silicates in cement. These gels are believed to be constructed of particles, which are plates or fibers, in contact only at certain points. This arrangement of flocculated particles leads to a loose three-dimensional network of solids in a liquid medium. Setting would occur when sufficient gel had formed to increase the yield values and viscosities of the pastes to a characteristic degree. Setting would also be aided by the removal of water by evaporation and by chemical reaction.

Tricalcium aluminates were found to increase the "strength" or consistency of the pastes. The rates of increase of the rheological coefficients were augmented by an increase in the temperature of hydration, alkai content and amount of initial mixing of the cement and water.

Résumé

Les comportements d'écoulement des pâtes fraîches ont été examinés dans le but d'obtenir des renseignements sur les propriétés en question et d'essayer de mettre celles-ci en corrélation avec la nature physico-chimique des pâtes. Des mesures rhéologiques furent opérées à l'aide d'un viscomètre à cylindre coaxial. Avec cet instrument des diagrammes de rotation-moment de torsion furent déterminés en fonction de différentes variables. Les diagrammes furent établis avec r.p.m. croissante (courbe ascendante) et r.p.m. décroissante (courbe descendante) en fonction de la moment de torsion. D'après ces diagrammes, des paramètres se rapportant aux valeurs de la limite d'écoulement f et aux viscosités plastiques U furent évalués. Parmi les variables étudiées se trouvaient: (1) les compositions chimiques des ciments (2) les conditions de mélange (3) les surfaces spécifiques des ciments et (4) la température d'hydratation.

Les données indiquaient que l'on trouve fréquement trois types de comportement rhéologique dans les pâtes: (1) antithixotropique (2) réversible et (3) thixotropique. Le comportement antithixotropique fut détecté dans les pâtes qui avaient été vigoureusement agitées et qui avaient pu s'hydrater quelque peu. Le comportement antithixotropique est caractérisé par une courbe d'écoulement (r.p.m.-moment de torsion) dans laquelle la portion descendante (r.p.m. décroissante) est á la *droite* de la courbe ascendante (r.p.m. croissante) Les courbes d'écoulement réversibles r.p.m.-moment de torsion étaient présentées par des pâtes qui avaient pu s'hydrater pendant 45 minutes environ. Le type de courbe d'écoulement prédominant était thixotropique. Les pâtes sont essentiellement thixotropiques dans le comportement d'écoulement avec les autres types qui sont surtout des déviations de ce comportement. La thixotropie est caractérisée par une courbe d'écoulement dans laquelle la branche descendante est à la *gauche* de la courbe ascendante.

Il est suggéré que la thixotropie est caractéristique de l'hydrogel formé par l'hydratation des silicates de calcium dans le ciment. On pense que ces gels sont formés de particules, qui sont des plaques ou des fibres, en contact seulement en certains points. Cet arrangement de particules floculées mène à un réseau lâche à trois dimensions de solides dans un milieu liquide. La prise se produit quand suffisamment de gel s'est formé pour augmenter les valeurs de la limite d'écoulement et les viscosités des pâtes à un degré caractéristique. La prise est également favorisée par l'élimination de l'eau par évaporation et par réaction chimique.

Les tricalciumaluminates augmentent la "résistance" ou consistance des pâtes. Les vitesses d'accroissement des coefficients rhéologiques étaient augmentées par l'accroissement de la température d'hydratation, la teneur en alcali et la quantité de mélange initial du ciment et de l'eau.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Ill.

Zusammenfassung

Das Fließverhalten frischer Pasten wurde mit dem Zwecke, mehr Kenntnisse über diese Eigenschaften zu erhalten, und auch für die Herstellung eines Zusammenhanges solcher Eigenschaften mit der physikochemischen Natur der Pasten, untersucht. Rheologische Messungen wurden mit Hilfe eines coaxialen Zylinderviskositätsmesser unternomnen. Mit einem solchen Instrument wurde das Drehmoment für verschiedene Umdrehungsgeschwindigkeiten als Funktion mehrerer Veränderlicher bestimmt. Kurven wurden für steigende Umdrehungsgeschwindigkeiten (die ansteigende Kurve) und für fallende Umdrehungsgeschwindigkeiten (die fallende Kurve), als Funktion des Drehmoments gezeichnet. Aus solchen Kurven wurden die Parameter, die zur Fließgrenze f und der plastischen Viskosität U gehören, ausgewertet. Zu den Veränderlichen, die untersucht wurden, gehörten: (1) die chemische Zusammensetzung des Zements, (2) die Mischbedingungen, (3) die Oberflächengrößen des Zements und (4) die Hydratationstemperatur.

Die Data zeigten, daß drei typische Fließverhalten häufig in Pasten gefunden werden: das (1) antithixotropische, das (2) umkehrbare und das (3) thixotropische Verhalten. Antithixotropisches Verhalten wurde in Pasten, die heftig gerührt worden waren und ein wenig Wasser binden konnten, beobachtet. Dieses Verhalten ist durch eine Fließkurve (Umdrehungsgeschwindigkeit-Drehmoment), bei welcher der fallende Ast (abnehmende Umdrehungsgeschwindigkeit) auf der *rechten* Seite der ansteigenden Kurve (zunehmende Umdrehungsgeschwindigkeit) liegt, ausgezeichnet. Die umkehrbaren Umdrehungsgeschwindigkeit-Drehmomentkurven wurden bei Pasten, die für ungefähr 45 Minuten hydratisieren konnten, gefunden. Die meisten Kurven gehörten der thixotropischen Art an, sodaß die meisten Pasten ein thixotropisches Fließbenehmen zeigen, und die anderen als Ausnahme von der Regel betrachtet werden können. Thixotropie kann durch eine Fließkurve, bei welcher der fallende Ast auf der *linken* Seite der steigenden Kurve liegt, erkannt werden.

Es wird vorgeschlagen, die Thixotropie als das Kennzeichen des Hydrogels, welches durch die Hydratation des Kalziumsilikats im Zement entsteht, anzusehen. Es wird angenommen, daß diese Gele aus Teilchen gebildet werden, welche Platten oder Fasern sind, und die sich nur an einigen Punkten berühren. Dieser Aufbau aus ausgeflockten Teilchen ergibt ein loses, dreidimensionales Gitter, welches aus festen Körpern, die von einer Flüssigkeit durchdrungen werden, besteht. Erstarrung wird dann einsetzen, wenn sich genügend Gel für die Erhöhung der Fließgrenze und der Viskositäten der Pasten in dem charakteristischen Grad gebildet hat. Eine Verdampfung des Wassers und chemische Reaktionen liefern zu dieser Erstarrung ihren Beitrag.

Es wurde gefunden, daß Trikalziumaluminate die "Festigkeit" oder die Konsistenz der Pasten erhöhen. Die Zuwachsgeschwindigkeiten der Fließkoeffizienten wurden durch eine Erhöhung der Hydratationstemperatur, des Alkaligehalts und des Betrags des ersten Mischens des Zementes mit Wasser vergrößert.

Introduction

Although a knowledge of the flow properties of portland cement pastes is essential to the proper use of concrete and to an understanding of its physicochemical nature, relatively little quantitative information on this subject has been reported. The present study was initiated in order to provide such information. In this paper there is described an investigation of the properties of these pastes in the first few hours of hydration.

Portland cement pastes are made by mixing water and cement in various ratios. The usual ratios by weight of water to cement, w/c, are between 0.3 and 0.7.

Cement is a material which is made up primarily of the following crystalline components sintered together into particles [1][1]: tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$), and tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). To this mixture, gypsum ($CaSO_4 \cdot 2H_2O$) is added.

Pastes are defined by Alexander and Johnson [2] according to the concentration by volume of solid particles in a liquid and by the flow properties. Usually the concentration in pastes is greater than 10 percent by volume. The systems exhibit elastic behavior and are plastic insofar as they show yield values. It is necessary to treat pastes as two-phase systems which are frequently thermodynamically unstable. Pastes are not discontinuously different from gels, since both states are characterized by intimate contact of the solid particles. Perhaps it is possible to distinguish between them by the particle size of the suspended particles. Gels are by definition made up of particles with colloidal dimensions and pastes normally contain particles in the micron range.

Engineers and workmen who make concrete structures are concerned with the flow properties of fresh concrete. Fresh concrete must flow sufficiently for proper placement.

In addition to these practical uses to which a knowledge of the rheology of the system may be put, there are many other matters that the flow properties can help to explain or control. The setting and hardening of concrete are caused by physical and chemical processes which produce a new material. Set concrete no more resembles the cement from which it was made than cement resembles limestone and clay from which it was made. If we are to understand what is meant by setting, which is manifested by a change in the flow properties of the material, then we must study the flow properties by the best scientific methods. It is because of the ease with which fresh concrete may be placed, and because of the mechanical properties of set concrete, that this material is so useful. The rates at which setting and hardening of concrete proceed affect seriously our ability to handle the material, and they affect the strength of the final product. To control the setting process, it will be necessary to understand: (1) the fundamental chemical processes proceeding in cement pastes, (2) the nature of the colloidal products formed, and (3) the forces exerted between hydrate particles.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The chemical reactions which proceed in concrete by reactions of cement and water lead to many hydrated products. The nature of these products is still being investigated. Perhaps the most important components of cement are $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$, which make up more than 70 percent of the material. When $3CaO{\cdot}SiO_2$ reacts with water, a hydrated calcium silicate and calcium hydroxide are formed. Similar hydrates are formed from β-$2CaO{\cdot}SiO_2$ [3]. The other components of cement react to form a variety of products [1].

The nature of the set hydrated cement has been examined for many years by Powers and his colleagues [4–6]. According to the results of their research it appears that on hydration of portland cement the surface of the solids increases from about 0.2 m^2/g to over 200 m^2/g. This shows that on hydration of micron-size portland cement, a colloidal material is formed. The colloidal product exhibits the properties of a gel. Measurements reported by Powers [6] demonstrate that the gel particles are separated by about 20 to 40 A. The gel would naturally consist mainly of hydrated calcium silicates since over 70 percent of the cement is composed of tri- and dicalcium silicates. Very little has been reported about the contributions of the other components to the gel structure.

A great deal of work has been performed to investigate the rheological problems mentioned here by methods which are semiquantitative [1]. Only a little attention will be given to this literature although the information provided by this research has materially benefited the field of cement technology [7]. In the present report only research based on modern theories of rheology and of colloid chemistry will be mentioned.

Reiner [8] has discussed the rheology of concrete. Apparently relatively few investigators were concerned with fresh pastes. Powers and Wiler [4] in an early paper outlined very well the problems involved in such a study, and proceeded to show the thixotropic nature of concrete at some stages of hydration.

Later Forslind [9] and L'Hermite [10] initiated investigations. More recently Dellyes [11], Papadakis [12], and Tattersall [13, 14] conducted research on pastes in coaxial cylinder viscometers essentially according to the methods outlined by Green [15].

In Green's method a coaxial cylinder rotational viscometer with variable speeds is employed. If a material is a Newtonian, a straight line relationship will be obtained for the plot of speed of rotation, Ω, against the torque, T. For Newtonians, the intercept on the torque axis will be at zero; however, for Bingham bodies and plastic materials the curve will intersect the torque axis at a value proportional to the yield stress, which is the minimum stress necessary to cause flow. The plastic viscosity, U, of the material in this procedure is inversely proportional to the slope of the linear portion of the rpm-torque plots.

The Green method for measurement calls for increasing the speed of rotation and then decreasing it in a prescribed manner. The corresponding torques measured in this way form an *upcurve* and a *downcurve* in a plot of speed of rotation against torque. If the material is thixotropic, the upcurve does not coincide with the downcurve; thus a hysteresis loop is formed. In this case the upcurve is concave towards the speed of rotation axis and the downcurve is in many cases a straight line, to the *left* of the upcurve. For standard conditions of operation, the area of the hysteresis loop, A, is related to the amount of breakdown of the thixotropic structure, and two successive cycles of this kind would define, according to Green, a quantitative parameter—"the coefficient of thixotropic breakdown".

For convenience in characterizing materials which are not Newtonians, but for which the downcurve portion of the flow curve is approximately linear, numerical values of yield stresses, f, and plastic viscosities, U, are evaluated from the linear portion of the rpm-torque curve using the Reiner-Riwlin equations [16, 17]. Strictly speaking, however, the lower portions of these curves do not conform to Bingham bodies with the calculated parameters.

Dellyes [11] and later Papadakis [12] did an excellent job of characterizing pastes of cements according to the rheological system of Green. Dellyes reported finding both thixotropy and a behavior which he defines as "antithixotropy" in some pastes. In antithixotropy, the descending curve falls to the *right* of the ascending curve—the opposite of the result for thixotropy. The nature of antithixotropy is unusual but may resemble the general behavior of concentrated pastes [18–20]. Many inorganic pastes show an increased resistance to flow with increased shearing stress. To some of these pastes the term "dilatant" is applied.

These authors reported the presence of the various types of rheological behavior present in fresh pastes. In addition, they demonstrated the influence of water-cement ratios on the rheological coefficients. Tattersall attempted to develop a quantitative picture for thixotropic breakdown.

Much work remains to be done to incorporate the knowledge of the rheological behavior of this system into the pattern now being developed for the physics and chemistry of the changes which occur during the hydration of cement. Also, much research is necessary before it will be possible to incorporate the empirical findings into the theories of Freundlich, Kruyt [21], and Verwey and Overbeek [22] for the behavior of gels.

Forslind [9] has developed a theory which is contrary to the current approach to gels, which explains the rheological properties of hydrogels on the basis of the water structure. According to this author, water behaves as if a structure existed in the water in contact with high-surface-area silicates. This structure, he believes, causes the observed properties. However, many other scientists [22] feel that it is the interaction of the solid particles which is the controlling factor. In the present paper the latter approach was adopted.

A number of difficulties are encountered in rheological studies on portland cement gels and pastes which limit the methods and the range of variables that can be examined.

(1) The rheological properties of the cement pastes are time dependent, antithixotropic, and thixotropic, and as such present the usual difficulties [17]. The structures of these materials change as they are disturbed. Therefore, in order to completely characterize the materials, it would be necessary to measure the flow properties at each stage of the structural transformations.

(2) The first item is even more serious, if the cement paste is hydrating during the study.

(3) At the beginning, rather large particles of cement are present. Therefore, sedimentation becomes a problem at high water-cement ratios.

(4) The large particle size of cement also prevents the use of cylinders with very small clearances in the coaxial cylinder viscometer and also the use of cone-plate viscometers.

Experimental

Materials

Pastes of a variety of commercially prepared portland cements were examined in order to observe the rheological behaviors and to try to correlate the differences in flow behavior with the variations in chemical composition. In table 1 the computed compound compositions and surface areas are listed. These cements were specially prepared and have been examined by many techniques in this laboratory.

The sample of alite was obtained from Dr. D. L. Kantro and Mr. C. H. Weise of this laboratory and the procedure for the preparation is described elsewhere [24]. This sample contains 0.75 percent free CaO, 0.88 percent Al_2O_3, and exhibits a surface area of 1,800 cm^2/g. The surface areas were determined by the Wagner turbidimetric method [25].

Preparation of Pastes

Standard procedures for the mixing of cement and water have been developed in order to obtain reproducible results. Some of the problems involved have been discussed by Powers [26].

In a typical procedure, 750 g of paste were mixed in a 1–3–2 min cycle of mix-rest-mix in a Waring Blendor under vacuum. Samples were mixed under vacuum in order to avoid the entrainment of air. The effect of air on the flow properties of pastes has been studied [27]. The cement powder was added gradually to the water with only a small amount of stirring. This step was followed by a vigorous mixing period. A normal procedure involved: (1) adding the cements to water with mild agitation, (2) 1 min of vigorous agitation and (3) 3 min of rest, followed by (4) 2 min of vigorous agitation. The effects of variations in this procedure will be described.

The temperature of the paste after the mixing procedure will be referred to as the final temperature; it normally was 25±2 °C. In some special experiments this final temperature was varied by adjusting the initial temperature of the water, or by the addition of ice.

The rheological measurements were made usually at 25 °C (with water jacket) after various periods of hydration t_h. Usually the samples were hydrated at a room temperature of approxi-

Table 1. *The computed compound compositions*

Composition, percent	A 15366 (*C* 2.2.7) Type I normal (clinker)	B 15367 (*C* 16.2.2) no gypsum	C 15698 (*C* 12.2.3) Type I normal	D 15669 (*C* 14.2.2) Type IV low heat	E 15622 A (*C* 13.2.3) Type II moderate heat	F 19648 (*C* 15.2.2) zero C_3A
C_3S	44.8	45.4	45.3	33.0	49.2	66.0
C_2S	26.9	28.5	28.6	54.2	28.5	14.7
C_3S/C_2S	1.67	1.59	1.58	0.61	1.73	4.5
C_4AF	6.7	6.8	7.6	5.8	12.8	10.15 (3.16% C_2F)
CaA	13.6	14.3	9.8	2.3	4.4	0.0
$CaSO_4$	3.3	0.7	3.0	3.1	2.7	4.30
MgO	2.5	2.63	3.4	1.72	1.44	0.60
Free CaO	0.93	0.98	0.08	0.15	0.49	0.58
Total alkali (Na_2O+K_2O)	0.33	0.33	1.57	0.27	0.22	0.12
Surface area, cm^2/g (Wagner turbidimeter)	2,260	1,500	2,250	2,280	2,200	2,640

mately 25 °C. However, in a series of experiments the pastes were allowed to stand at temperatures between 20 and 35 °C in a constant temperature bath to examine the effects of the temperature of hydration on the rates of changes of rheological properties.

Apparatus

Viscometer—General

Various rotational viscometers have been used for the investigation of the rheology of portland cement pastes, but most of them resemble closely the viscometer developed by Green [15]. In this study the Haake Rotovisco instrument designed by Heinz was employed [23]. The instrument was calibrated with oils of known viscosities.

With a concentric cylinder viscometer, the angular velocity of the bob, Ω, in rpm, and the torque, T, in dyne-cm, are measured. In the Rotovisco instrument, the bob of radius r_0 and length h may be rotated at various angular velocities, Ω, in a sample contained in a stationary cup of radius R_0. A substance of viscosity η is inserted in the annular space between the bob and cup. Because of the viscosity of the material, a torque, T, is required to maintain each velocity.

The torque developed causes a spring attached to the bob to wind up. The displacement of the spring is converted by an electrical device to a reading on a meter. The combination of motors and gears makes it possible to obtain the following bob speeds: 3, 6, 9, 18, 27, 54, 81, 162, 243, and 486 rpm at a line frequency of 50 c/s. At the line frequency of 60 c/s used in the present study the speeds are increased by a factor of 6/5.

In the Rotovisco apparatus the cup is 2.102 cm in radius, and the bob used has a radius of 1.999 cm. The length of the bob is 6.0 cm. To reduce the end effect at the bottom of the bob, a recess is provided to entrap an air cushion. A water jacket fits over the cup, and water at a constant temperature is passed through it. The temperature of the water in the jacket is referred to as the temperature of the measurement.

The equation for the flow curve of a plastic Bingham body is

$$(\tau - f) = U\dot{\gamma} \tag{1}$$

where τ is the shearing stress, $\dot{\gamma}$ is the rate of shear, f is the yield value or yield stress, and U is the plastic viscosity.

Reiner and Riwlin [16] derived the relationship for the flow of a Bingham body in a rotational viscometer.

$$\Omega = \frac{T}{4\pi U h}\left(\frac{1}{r_0^2} - \frac{1}{R_0^2}\right) - \frac{f}{U}\ln\frac{R_0}{r_0} \tag{2}$$

when the total torque is sufficient to exert a shearing stress that exceeds f at the inner surface of the cup of radius R_0.

Usually the velocity of the bob, in revolutions per minute (rpm), is measured versus the deflection S of the meter and a plot of these quantities forms the flow curve. From the slopes and intercepts and the calibration constants of the instrument, the values of f, U, and A are calculated.

Results

Results of a Typical Fresh Cement Paste and Definition of Terms

Figure 1 is a schematic plot of the results on a Type I cement (A), and will be used to point out their characteristic features. Table 2 summarizes a set of actual data. Curves A, B, and C are plots of rpm against torque. They were obtained for identical samples at successively longer times of hydration. In each one of these sections, results of two successive cycles are drawn in: (1) denoting the first cycle and (2) the second. The second

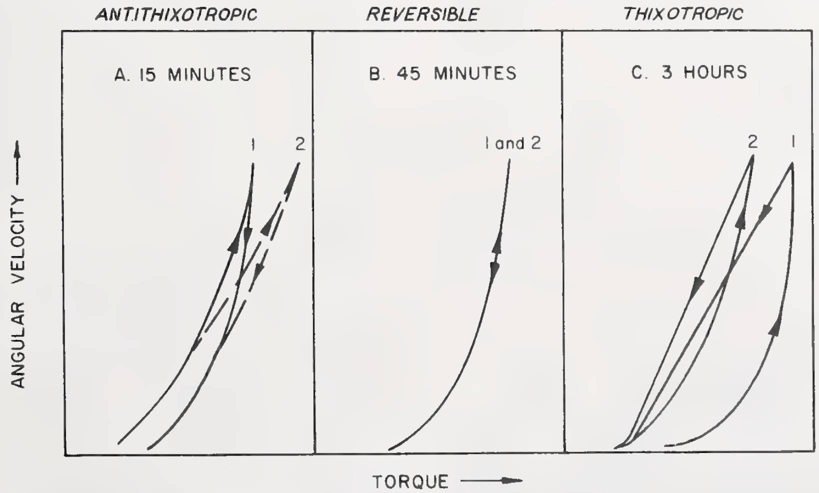

FIGURE 1. *Three types of flow behavior for fresh portland cement pastes.*

The times given are for the periods of hydration. The numbers on the curves show the order in which the curves were made.

cycle represents a flow curve obtained immediately after the first cycle is completed.

In curve A, the downcurve in each cycle is to the right of the upcurve, and the second cycle is to the *right* of the first one, indicating an increase in viscosity. Exactly the reverse holds in C. However, both are similar in that the area of the hysteresis loop, *A*, is smaller in the second cycle than in the first one. The curve shown in B is *reversible:* i.e., the upcurves and downcurves in both the first and second cycle coincide.

For convenience in communication, these characteristics of rheological behavior are assigned names on a *strictly operational* basis. The curves shown in C are examples of thixotropy [15].

The fact that successive cycles in C decrease the area of the loop and move it to the left tends to show that, at best, the process of spontaneous buildup of a thixotropic structure is very slow. Some comparative measure of the *amount* or *extent* of thixotropic breakdown can be derived from the area of the hysteresis loop, *A*, obtained under specific conditions.

TABLE 2. *Results of an experiment with a typical type I portland cement paste*

(Cement A (Sample *C* 2.2.10); w/c=0.5; final temperature 24 °C; hydrated in a water bath at 25.0±0.2 °C)

Time of hydration	Temp. of sample	First cycle			Second cycle	
		Yield Value *f*	Plastic Viscosity *U*	Area of hysteresis loop *A*	Yield value *f*	Plastic viscosity *U*
	°C	*dynes/cm²*	*cp*	*arbitrary units*	*dynes/cm²*	*cp*
15 min	25.0	445	24	−25	440	26
45 min	25.4	560	25	−12	560	25
2 hr	25.8	990	54	600	900	51
3 hr	26.0	1,340	93	>730	1,170	68

The behavior shown in A is less common. Dellyes [11] referred to this behavior as "antithixotropy" since it shows a contrasting behavior to "thixotropy". A measure of its extent can also be given by the area of the hysteresis loop. In order to unify the description, the areas of the hysteresis loops are *defined* as *negative* if the downcurve is to the *right* of the upcurve, and are *defined* as *positive* if the downcurve is to the *left* of the upcurve. It is thus possible to describe the extent of antithixotropy and thixotropy in terms of the areas of the loops.

Both antithixotropy and thixotropy have been observed in quite a number of cases in our work, but the reversible case in between was found only occasionally. Its presence between the two extremes might, however, be expected.

It should be pointed out that the use made in this paper of the actual values of *A* is only as a rough comparative measure of the availability of breakable structure in the system.

Small changes in the conditions of handling the pastes on insertion into the viscometer were found to cause relatively large changes in the loop areas, *A*, particularly after 3 hr of hydration. At this time the degree of thixotropic behavior was much greater than that at earlier periods. The values of *A* reported indicate trends very well.

Because of the relatively rapid physicochemical changes proceeding in the pastes, it was initially felt desirable to make the measurements as rapidly as possible. Further investigation demonstrated that the changes occurred at a much slower rate than was initially expected.

In general, the data show that the results are reasonably reproducible if the methods for handling the samples are the same.

The Effect of Cement Concentration

A Type I cement (A, table 1) with a surface area of 2,260 cm²/g was used. The range of water-cement ratios by weight was 0.4 to 0.8. In this series of measurements the whole batch was kept after preparation in a plastic container at room temperature. Samples were drawn from it for rheological measurements at 15 min, 45 min, and 2 hr of hydration. The measurements were made in the Rotovisco without the water jacket.

The results are shown in table 3. The volume percent of solids was calculated assuming the density of the cement to be 3.2 g/cm³, and that of water to be 1.0. The values of the parameters *U*, *f*, and *A* at the same time of hydration may be seen to increase rapidly with increase in concentrations of solids.

TABLE 3. *Rheological parameters of portland cement pastes of various water-cement ratios at different times of hydration*

Designation of sample	w/c	Volume fraction of cement	Final temperature	Time of hydration	First cycle			Second cycle	
					f	U	*A*	f	U
			°C		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*
C 1.1.2	0.4	0.439	23	15 min	810	39	0	------	----
				40 min	970	52	15	970	48
				2 hr	------	------	Very large	1280	79
C 5.1.1	.45	.410	21	15 min	390	22	18	390	26
				45 min	405	26	22	390	26
				2 hr	810	100	530	820	70
C 2.1.2	.5	.384	16	8 min	250	16	−9	260	17
				30 min	250	16	−10	268	15
				2 hr	340	42	133	340	32
C 4.1.1	.6	.342	20.5	15 min	90	12	−3.2	100	12
C 3.1.2	.7	.307	19.5	15 min	64	8.5	−6	71	8.5
				45 min	52	7.4	0	52	7.4
				2 hr	77	12	29	77	10.3
C 7.2.2	.8	.280	17	15 min	16	5.8	0	16	6.1

Figures 2 and 3 are plots of the plastic viscosity U/U_0 and yield stress f/f_0 in the first cycle against time of hydration. U_0 and f_0 are the values of the plastic viscosity and yield stress after 15 min of hydration. From these figures it may be seen that the *rate of development* of the consistency increases rapidly with increase in the concentration of solids.

The rapid increase in the area of the hysteresis loop, *A*, at 2 hr hydration time with increase in concentration of solids is evident from the data in table 3.

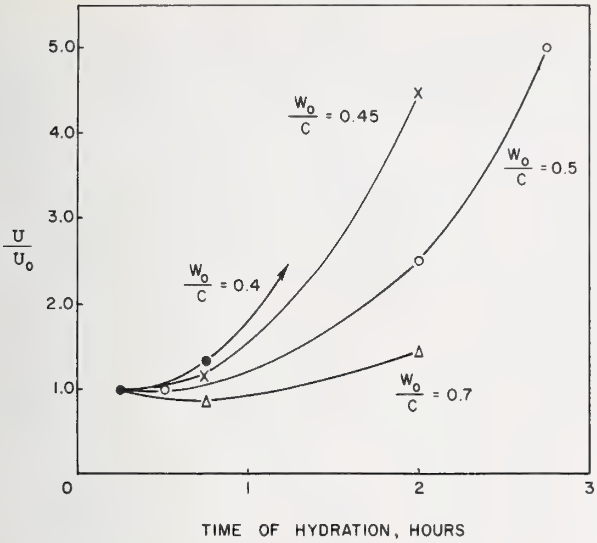

Figure 2. *Plot of plastic viscosity against time of hydration for various water-cement ratios.*

U_0 is the plastic viscosity of the various samples after 15 min of hydration.

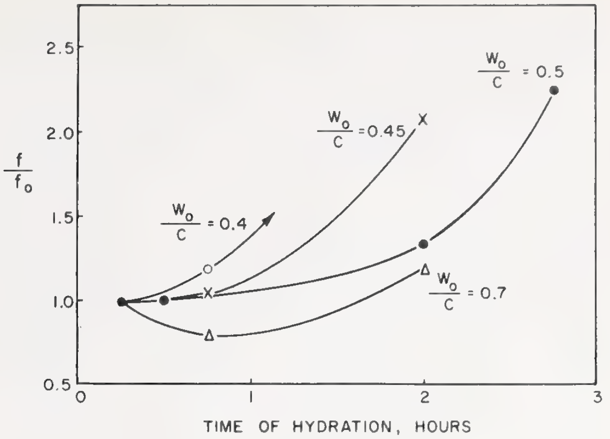

Figure 3. *Plot of yield values against time of hydration for various water-cement ratios.*

f_0 is the yield value for the various samples after 15 min of hydration.

Effect of the Temperature of Hydration

The development of the rheological properties is presumably related to the chemical reactions proceeding in the pastes. Chemical reactions would be expected to increase in rate with temperature. The relationship between the rate of development of the rheological properties and the rate of the chemical reactions is not known. The details of the chemical reactions at these early stages are not entirely clear either. Nevertheless, it is of interest to examine the development of the rheological properties at various temperatures of hydration. A type I cement, A, was examined. Four preparations were made for hydration at 20, 25, 30, and 35 °C. The temperatures of the samples before measurement are listed in column 4 of table 4, which summarizes the results. It may be noted that the sample temperatures deviated from the temperature of the bath in which they were immersed. These deviations were due to the time it took for the samples, which had a final temperature of 25 °C after mixing, to reach the temperature of the bath and also to the heat released during the chemical reactions.

The results do not apparently exhibit, in general, very large effects on the plastic viscosities, *U*, yield stresses, *f*, and the areas of the loops, *A*. The yield values at 15 min hydration time did not show appreciable differences between 20 and 35 °C hydration temperatures, but after 2 hr of hydration an increase in yield stress of 890 to 1,340 dynes/cm^2 was noted when the hydration temperature rose from 20 to 35 °C. A similar trend of increases in plastic viscosities may be seen in table 4. A plastic viscosity of 48 cp after 2 hr of hydration at 20 °C may be compared to the 157 cp found after hydration for the same period of time at 35 °C. A similar rate of increase in the extent of thixotropic behavior may be found. The value of *A* after 2 hr of hydration at 35 °C is over 1,150 compared to the 320 measured on a sample hydrated for the same period at 20 °C.

A *small* increase in the rate of development of the rheological coefficients with temperature would be consistent with the theory that after the initial mixing of cement and water the reaction rate is diffusion controlled. Obviously more information on the dependence of rates of the chemical reactions on temperature is necessary before these data can be fully understood.

Table 4. *Effect of temperature of hydration*

Designation of sample	Temperature of hydration	Time of hydration	Temp of sample before measurement	*f*	*U*	*A*
	°*C*	t_h	°*C*	*dynes/cm²*	*cp*	
C 2.2.12	20.0	15 min	23.5	460	24	−19.3
		45 min	20.8	560	23	−28.8
		2 hr	20.8	890	48	320
		3 hr	20.7	1340	101	>666
C 2.2.10	25.0	15 min	25.0	445	24	−24.5
		45 min	25.4	560	25	−11.9
		2 hr	25.8	990	54	600
		3 hr	26.0	1340	93	>730
C 2.2.13	30.0	15 min	28.8	500	25	−26.8
		45 min	30.5	600	32	33.2
		2 hr	30.8	1240	150	630
		3 hr	31.6	Too high to measure.		
C 2.2.9	35.0	15 min	34.0	480	33	−56.3
		45 min	35.7	680	35	30.7
		2 hr	36.5	1340	157	>1150
		3 hr	----------	Too high to measure.		

Effect of Surface Areas of Cements

An increase in surface areas of the cements would be expected to increase the rate of hydration. To explore the effects of this variable, a Type I cement of composition A (table 1) with surface areas of 2,260 cm^2/g (15,366) and approximately 1,700 cm^2/g (15,365) were made into pastes with w/c ratios of 0.5 and 0.45. The results are summarized in table 5.

The higher surface area cements, for *both* w/c ratios, seemed in general, to exhibit higher yield stresses, plastic viscosities, and extents of thixotropy than the samples with the lower surface areas.

The greater activity of the higher surface area cement is demonstrated in the development of heat in the pastes. At w/c=0.5 the final temperatures were 26.5 and 25.3 °C for the 1,700 cm^2/g and the 2,260 cm^2/g samples, respectively. Upon hydration the temperatures of the 1,700 cm^2/g samples were 26.8, 26.8, 26.8, and 27.1 °C at 15 min, 45 min, 2 hr, and 3 hr of hydration, respectively. The corresponding temperatures of the 2,260 cm^2/g samples were 26.0, 26.2, 26.8, and 28.2 °C, respectively. The more rapid rise in the temperature of the higher surface area materials as compared to that of the lower surface area materials is evident from these values.

Table 5. *Effect of specific surface of cements on the rheological properties of the pastes made therefrom*

	Time of hydration t_h	2,260 cm^2/g (*C*2.2.7)			1,700 cm^2/g (*C*6.2.1)		
		f	*U*	*A*	*f*	*U*	*A*
		dynes/cm²	*cp*		*dynes/cm²*	*cp*	
w/c=0.5	15 min	260	23	−10.6	200	19	0
	45 min	290	31	0	220	28	0
	2 hr	510	39	290	340	38	10.6
	3 hr	850	195	>800	500	58	176
		2,260 cm^2/g (*C*5.2.2)			1,700 cm^2/g (*C*11.2.1)		
w/c=0.45	15 min	770	47	−14	--------	--------	--------
	45 min	1,060	53	5.2	540	56	10
	2 hr	([a])	([a])	([a])	860	68	40.8
	3 hr	([a])	([a])	([a])	([a])	([a])	([a])

[a] Too high to measure.

The Rheological Properties of Various Cements

In most of this work on the rheology of fresh portland cement pastes, a single Type I cement (A, table 1) was used. The purpose of the series of experiments reported in this section was mainly to determine whether the rheological behavior that has been observed was typical of the specific cement used or was characteristic of fresh portland cement pastes, in general. In addition to that, it was desirable to get some information about the effects of chemical composition of the cements on the rheological behavior of the fresh pastes. For this purpose samples of cement (table 1) of Types I (A), II (E), and IV (D) were examined at w/c=0.5, as well as a sample of low gypsum content (B), one of high alkali content (C), and one of alite.

Samples were prepared in a Waring Blendor under vacuum, using a 1–3–2 min of mix-rest-mix procedure. The final temperatures were maintained at 25±2 °C, except for the cases of low gypsum content and of alite, in which cases the temperatures were 20 and 33 °C, respectively. The hydration took place in closed plastic containers at room temperature and the rheological measurements were made on the undisturbed samples at 15 min, 45 min, 2 hr, and 3 hr after preparation.

The compositions of the cements are shown in table 1, and the results of the rheological measurements are listed in table 6. In general, the data show that the samples all develop some thixotropy, but certain variations in the details of the flow are evident.

Table 6. *Rheological properties of various cements*
(w/c=0.5)

Time of hydration t_h	*f* *dynes/cm²*	*U* *cp*	*A*	*f* *dynes/cm²*	*U* *cp*	*A*
	A 15366 (*C*2.2.7) Type I Normal			B 15367 (*C*16.2.2) No Gypsum		
15 min	260	23	−10	630	110	1,290
45 min	290	31	0	540	93	1,130
2 hr	510	39	290	780	140	>950
3 hr	850	195	>780	430	120	1,300
	C 15698 (*C*12.2.3) Type I Normal			D 15669 (*C*14.2.2) Type IV Low Heat		
15 min	270	29	0	120	15	−5
45 min	330	28	−36	130	17	9.7
2 hr	840	56	145	140	19	32
3 hr	2,110	110	>530	200	31	145
	E 15622A (*C*13.2.3) Type II Moderate Heat			F 19648 (*C*15.2.2) Zero C_3A		
15 min	100	15	5.1	100	23	47
45 min	110	17	15.0	140	28	86
2 hr	160	24	88.0	190	34	110
3 hr	280	53	>220	230	45	154
	G (*C*17.1.1) Alite (C_3S)					
15 min	16	16	16			
45 min	48	26	86			
2 hr	160	80	620			
3 hr	160	120	810			

Tricalcium aluminate, tricalcium silicate, the calcium sulfates, and alkali have been reported to contribute a great deal to the properties of fresh pastes. The effects of each of these constituents will be examined.

Figures 4–6 show, respectively, the changes in yield stress, *f*, plastic viscosity *U*, and the extent of thixotropy or antithixotropy, *A*, as a function of the calculated calcium aluminate content.

In figure 4 the yield values for cements A, D, E, and F may be seen to rise with the aluminate content (above about 4 percent C_3A content) for the 15-min, 45-min, 2-hr, and 3-hr hydration periods. The letters representing the cements appear above their respective positions on the curves. The Type I, high alkali cement C, exhibited the same general increase with time, but the *f* values were much higher than those shown in the curves. Cement B exhibited *f* values (table 6) which were not in accord with the general trend of increasing with time of hydration.

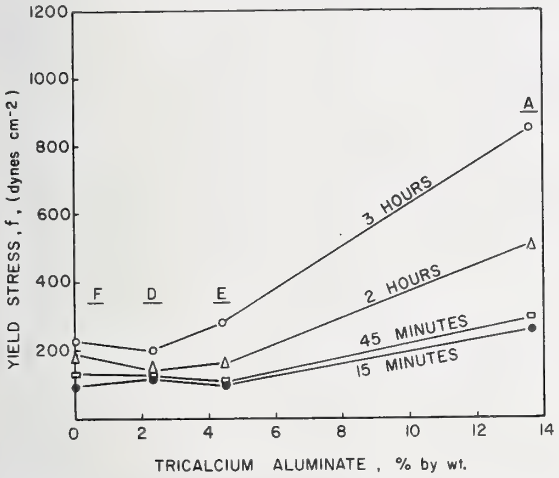

FIGURE 4. *Yield stress,* f, *as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

In general, figure 5 shows an increase of plastic viscosity with tricalcium aluminate content (above about 4 percent C_3A content) and hydration time. It may be noted, however, that both cement F and alite, which contain small amounts of tricalcium aluminate, deviate somewhat from the general trend. These cements, however, contain large proportions of tricalcium silicate. Cement B, with a low gypsum content, exhibits plastic viscosities which do not change markedly with hydration time but show substantially higher plastic viscosities.

Figure 6 demonstrates that cements A, D, E, and F show an increase in extent of thixotropy with increase in tricalcium aluminate content after 2 hr of hydration. On the other hand, alite with only 0.88 percent Al_2O_3 shows a much more rapid increase in extent of thixotropy with time of hydration. Cement B, which contains only 0.7 percent $CaSO_4$, demonstrated the most rapid development of thixotropy even after 15 min of hydration (table 6).

General trends of *f*, *U*, and *A* values with the calculated tricalcium silicate contents were not observed. This might be expected since the silicate contents of the cements are high and other components may affect the properties to larger extents than the variations in silicate content.

The effect of the other constituents on the extent of thixotropy is, however, less clear. The alite and the high tricalcium aluminate sample A both develop large extents of thixotropy while samples with intermediate contents of tricalcium aluminate develop much less of it. Obviously, there may be large differences in the nature of

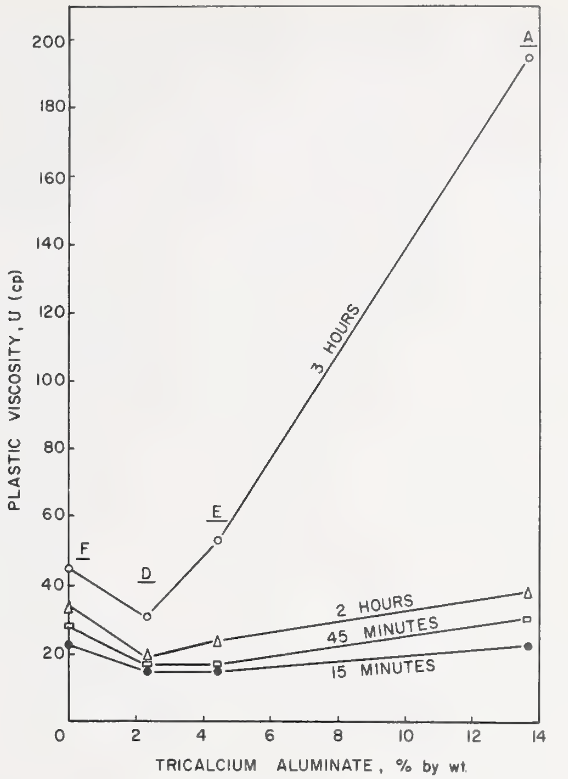

FIGURE 5. *Plastic viscosity,* U, *as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

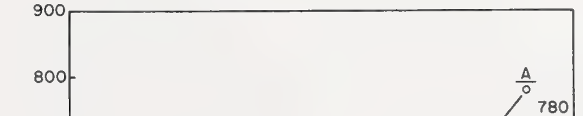

FIGURE 6. *Extent of thixotropy as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

thixotropy between these two extremes, which cannot be detected by comparing values of A alone.

It has been apparent in the experimental work that the influence of the minor components is marked. Their influence on the rates of chemical reactions, on the nature of the products, and on the electrolyte concentrations in solution would be expected. It may be assumed that the ions in solution influence strongly the interactions of both the hydrate and cement particles.

Cements A and B were made from the same clinker except that no gypsum was added to B, which therefore is simply clinker. The behavior of cement B on mixing differed substantially from those of the other cements. Within the 3-min rest period it stiffened considerably. The subsequent mixing was not efficient for this reason. The paste of cement B may be seen in table 6 to exhibit thixotropic properties after 15 min of hydration, but the relatively high yield values, and plastic viscosities did not change appreciably over 3 hr of hydration time. This behavior was in contrast to that of the paste of cement A which developed from an antithixotropic material to a thixotropic one during the 3 hr of hydration and the f and U values increased with hydration time. The behavior of cement B with no added gypsum is probably characteristic of what is referred to as "flash" set [7].

It is also possible to compare the behavior of cement F with that of alite. Alite and cement F contain no tricalcium aluminate but the latter contains 4.3 percent $CaSO_4$, whereas in alite there is no sulfate. Both F and alite pastes developed thixotropic behavior with no indication of antithixotropy. The extent of thixotropy in the paste of alite was greater than for paste F. Although the yield values of paste F were greater than those for the alite paste after 45 min hydration, the reverse is true for the plastic viscosities.

Pastes made from cements A and C differ mainly in their alkali and free CaO contents. The free CaO contents are 0.93 and 0.08 percent for cements A and C. On the other hand, cements A and C contain 0.33 and 1.57 percent total alkali, respectively. The difference in the tricalcium aluminate contents, i.e., 13.6 percent for A and 9.8 percent for C, would not be expected to cause much difference in properties (figs. 4, 5, and 6). An examination of the rheological behaviors of pastes A and C does show (table 6) substantial differences.

The Effects of Mixing Conditions

The changes in the characteristics of portland cement pastes in the first few hours of hydration may be expected to be rather sensitive to the conditions of mixing of the ingredients. In most of the work the 1–3–2 min of mix-rest-mix procedure in a Waring Blendor under vacuum was used. The purpose of the experiments reported in this section was to obtain some information about the effects of mixing on the rheological properties of the fresh paste.

In the present series of experiments the Waring Blendor under vacuum was still used, but variations were made in the time of mixing, procedure of mixing, and final temperature after mixing, and there was some variation in the temperature of hydration. All samples were prepared with w/c=0.5. Cement A was used. The rheological measurements were made on the undisturbed samples at 15 min, 45 min, 2 hr, and 3 hr after preparation.

The following experiments were performed.

(1) *1–3–2 min mix-rest-mix.* A normal run was made, with 1–3–2 min mix-rest-mix, controlling the final temperature to 25±2 °C. The samples were kept in a water bath at 25.0±0.2 °C until viscometric measurements were made.

(2) *Time of mixing.* Four separate preparations were made with 1, 3, 6, and 10 min of continuous mixing. The final temperatures were 25 °C. The samples were kept undisturbed in the room until rheological measurements were made.

(3) *Final temperature.* Three batches were made by 3 min continuous mixing, allowing the final temperature to attain values of 15.8, 23.2, and 34.5 °C. The samples were subsequently kept in a water bath at 25.0±0.2 °C until the measurements were performed.

Table 7 summarizes the results obtained when a 1–3–2 mixing schedule was compared with a 3 min continuous mixing period. It is worth while noting that the values of A for the cases of antithixotropy ($A<0$) are rather *small* relative to the values of A for the cases of thixotropy ($A>0$).

The values of the plastic viscosities are not significantly different from each other. However, comparing the values of A and f in both runs, one notes significant differences. In experiment 1 the values of f are *higher* and those of A *lower* than the corresponding ones in experiment 2.

The results did not show any appreciable effect of the final temperature after mixing although the differences between the final temperatures after mixing were rather large, 15–35 °C.

Table 7. *Comparison of effects of variation in mixing conditions*

Time of hydration t_h	Expt. 1 ($C2.2.10$) 1–3–2 mixing			Expt. 2 ($C2.4.6$), 3 min mixing		
	f	U	A	f	U	A
	dynes/cm²	*cp*		*dynes/cm²*	*cp*	
15 min	450	24	−25	310	25	−9
45 min	560	25	−12	350	29	19
2 hr	990	54	600	650	58	650
3 hr	1340	93	730	860	90	880

From all our experiments with cement pastes, the natural trend (within the first 3 hr at least) has been for the system to increase in thixotropy with time of hydration, as well as in "strength", as measured by the increasing value of the yield stresses f. From the data it appears as if the omission of the 3-min rest period in experiment 2 *enhanced* the development of thixotropy and *retarded* the development of "strength".

Table 8 summarizes the results for the four preparations in which the time of continuous mixing was varied from 1 to 10 min.

It is apparent from the table that the plastic viscosities tend to increase with an increase in the mixing time, and so do the yield stresses. From the values of A at 15 min of hydration, it is obvious that thixotropy does have a tendency to develop rather early, but is broken down by further mixing. This is also consistent with the relative values of A at 15 min of hydration shown in table 7. They are −9 for 3 min of continuous mixing and −25 for the 1–3–2 mixing schedule. The thixotropy developed during the 3 min of rest has been efficiently broken down by the subsequent 2 min of mixing, allowing more antithixotropic behavior to appear.

Table 8. *The effect of time of continuous mixing on the rheological behavior of fresh cement paste*

Time of hydration t_h	Sample C2.3.3 1-min mix			Sample C2.4.5 3-min mix			Sample C2.5.7 6-min mix			Sample C2.6.3 10-min mix		
	f	U	A	f	U	A	f	U	A	f	U	A
	dynes/cm²	*cp*		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*	
15 min	220	21	25	400	24	−6	490	29	−19	520	47	−66
45 min	210	24	21	460	25	0	570	34	0	680	38	~4
2 hr	310	39	192	730	53	550	670	42	130	1,490	86	~700
3 hr	480	84	620	940	59	~840	1,720	111	>750	1,950	119	>670

Discussion

Much additional research will be necessary on the rheology of fresh pastes before all the factors which control the flow properties will be understood. Nevertheless, an attempt will be made here to correlate as much information as possible into a picture of the physicochemical nature of the pastes. In order to do this many assumptions must be made.

At the present time, it is believed by many research workers [1] in this field that portland cement hydrates by solution and diffusion mechanisms. When portland cement is mixed with water, it appears that the solution immediately becomes supersaturated with respect to hydrated silicates and aluminates and calcium hydroxide. From this supersaturated solution the products of hydration precipitate as a gel around the unhydrated particles. After these initial solution reactions, further hydration proceeds by diffusion through the gel. These hypotheses are supported by several pieces of evidence.

One is that the solution phase immediately after mixing cement with water is saturated with respect to hydrated calcium silicate and supersaturated with respect to calcium hydroxide [31]. Another piece of evidence in support of the above theory of hydration was obtained from sedimentation studies. Powers [26] has reported that the sedimentation rate of cement in water does not change over the first hour of hydration. This behavior indicates that the particle sizes and numbers do not change appreciably in the early stages of hydration. Therefore, it is possible to conclude that the hydration in the early stages causes a gel layer to form around the cement particles without appreciable change in the size or number of active particles.

The major components (table 1) of portland cement are tricalcium silicate, dicalcium silicate, and tricalcium aluminate. The effect of the tetracalcium aluminoferrite on the flow properties is not well understood [7]. In order of rate of hydration [32], tricalcium aluminate is most rapidly hydrated, tricalcium silicate is next, and dicalcium silicate hydrates relatively slowly. In cements to which gypsum has been added, some hemihydrate of calcium sulfate is usually formed in the process of grinding the clinker with gypsum [33]. Varying amounts of alkali are found in portland cement. In the literature [7], many effects have been attributed to alkali.

It is reasonable to assume that the principal products of hydration of cement up to 3 hr are formed by the reaction of tricalcium silicate and aluminate. The hydration of calcium sulfate hemihydrate also proceeds rapidly. In order to have some quantitative notion about the chemical changes that have proceeded in the first 3 hr of hydration, it is worth while estimating the degree of hydration of these components. According to the data obtained in the present study and those derived from the literature [34], it appears that about 5 percent of portland cement hydrates in 3 hr. This estimate is based on the degree of hydration of the principal components. Thermobalance results in our laboratory show that about 6.5 percent of alite hydrates in 3 hr. Since about 45 percent of the cement is alite (A, table 1) then this would amount to about 3 percent hydration of the cement. According to Copeland, Kantro, and Verbeck [34] about 10–20 percent of the tricalcium aluminate hydrates in about 2 hr. If we assume that 15 percent hydration occurs in 3 hr, and we know that about 13.6 percent of the cement (A, table 1) is tricalcium aluminate, then this corresponds to an additional 2 percent hydration of the cement. Ershov [32] reported that considerable hydration of the aluminate occurs.

From a separate study of the composition of the aqueous phases in contact with portland cement it appears that the aqueous phase does not change appreciably with time. Apparently in the case of normal Type I cements the *p*H values and calcium ion concentrations remain relatively constant over the first few hours of hydration. The *p*H in this period of hydration was approximately constant at 12.8. However, the calcium ion concentration increased from 0.031 to 0.033 *M*, which may very well be within experimental error.

Since tri- and dicalcium silicate make up 70–80 percent of portland cement, it is not unexpected that the mechanical strength of set hydrated cement should be due almost entirely to the contribution made by them. Therefore, the nature of the contributions made by these components will be reviewed first. Certain conclusions which have been drawn on the basis of research on pure tricalcium silicate or alite, or dicalcium silicate or belite *may* not be valid for the hydration of alite and belite in portland cement. Nevertheless, until this information is available on the cement system, we shall use the available information on the pure components. The hydration of tricalcium silicate leads to products [3] which are in the form of plates and needlelike crystals. Some authors believe the fibers or needlelike crystals are formed by rolling up of the plates. Let us assume for simplicity that these particles are either fibers or plates [35].

At this point in the discussion it would be convenient to propose a structure for the calcium silicate hydrogel which forms on hydration of the silicates. The hydration of alite leads to a product which is thixotropic at all stages (table 6). According to current theory [22] thixotropic gels are made up of particles which touch at certain points only. For example, van Olphen [36] has proposed that bentonite gels form contact points between the negative charges on the surfaces of the plates and the positively charged edges. Such a structure would be like that shown in figure 7. The negatively charged surfaces may be there because of the presence of silanol groups, SiOH, which ionize in alkaline solution to SiO^- species. The positive charges van Olphen proposed are due to unsatisfied Al^{+++} charges at the edges of the plates. Bentonite gels are relatively strong structures at low concentrations of solids because of this network arrangement of the particles and the strong and numerous bonds [37] between the particles.

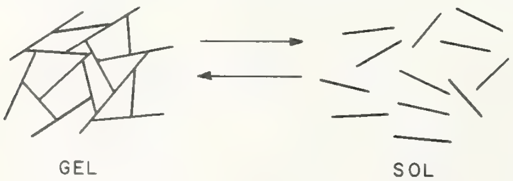

FIGURE 7. *Thixotropic system.*

It is possible to assume that a similar structure exists in hydrated cement except that large particles of unreacted material, calcium hydroxide, etc., are dispersed in the gel. According to the sedimentation studies of Powers [26] the gel is apparently densest around the cement particles.

The forces between the particles in the pastes are van der Waals and electrostatic forces. Zhuravlev and Tikhonov [38] and Reshetnikov [39] have reported that the solid hydrate particles in portland cement pastes exhibit a positive surface charge. By change in *p*H and ionic strength of the aqueous media in contact with solid surfaces, it has been found possible by Kruyt and his coworkers [21] to change the forces of attraction and repulsion between particles in thixotropic gels. The detailed nature of the forces between hydrate particles is not known.

To exhibit thixotropic properties, the forces between the particles must be sufficiently strong to hold the system together with a relatively low concentration of solute particles, but the forces must not be so strong that a small shearing stress will not break the bonds and cause a sol to form (fig. 7). The gel will reform when the sol is allowed to stand for a sufficiently long time. It must be pointed out, however, that after a portland cement paste, which has been hydrated to some extent, is agitated, the gel does not recover its original behavior. It has been reported [40] that strong agitation of a partially hydrated concrete mixture leads to a weak product.

Tricalcium silicate, portland cement, and mixtures of calcium oxide and pozzolanic materials, made up primarily of silica, hydrate to produce hard, strong products. On the basis of present information it is reasonable to assume that the hydrated silicates in these products exhibit the same properties.

The processes of setting and hardening probably consist of two factors. First, when sufficient calcium silicate hydrogel forms, the system exhibits large yield values and plastic viscosities. A study of calcium silicate hydrogels [41] shows that the yield values and plastic viscosities rise rapidly in the range of concentrations above 5 percent.

Reiner [8], in a review of the rheology of concrete, points out that the reduction of water content by evaporation and chemical reaction increases considerably the concentration of solids. Also, according to Powers and Brownyard [5], much of the free water is adsorbed on the large surface of the hydrate particles.

Whether or not chemical bonds form between the thixotropic gel particles (fig. 7) during setting is not clear. Such bonds could form through calcium ions or by condensation of silanol groups, SiOH. Copeland [34] has found that although it is difficult to disperse portland cement pastes even by ultrasonic techniques, tri- and dicalcium silicate pastes may be dispersed. Perhaps these results indicate that the bonds are stronger in cement pastes than in silicate pastes because there are chemical bonds in cement paste gels.

Cement F with no tricalcium aluminate shows no antithixotropic behavior and only relatively small degrees of thixotropy compared to alite or Type I cement pastes (A and C). The rapid rise of thixotropy within 15 min and the extent of thixotropic behavior (where A is approximately 1,300) shown by cement B which contains only 0.7 percent calcium sulfate seem to indicate that the hydration of the silicates and of the aluminates both lead to a higher degree of thixotropic behavior. Whether or not the hydrated aluminates alone form thixotropic structures is not known yet. It is reasonable to assume that cement B to which no gypsum was added undergoes "flash" set to some extent. This kind of set apparently leads to high yield values, >540 dynes/cm^2, plastic viscosities, >93 cp and extents of thixotropy of 1,130 even after 45 min of hydration.

When pure tricalcium aluminate reacts with water an immediate set results. This is commonly referred to as "flash" set. The introduction of gypsum into cement prevents the formation of "flash" set by forming, instead of the aluminate hydrate, a sulfoaluminate when the sulfate content is high.

It is perhaps reasonable to assume that the increase in yield values, plastic viscosities, and thixotropic development with tricalcium aluminate content in cements may be attributable to the formation of cross links in the silicate gels by the needle crystals of ettringite. It has been reported [7] that tricalcium aluminate increases the strength of set hydrated cement in the early stages. Budnikov [45] attributes the increase in strength to the sulfoaluminate crystals. If the tricalcium aluminate hydrates rapidly then it is also possible to attribute the increase in rheological coefficients to a removal of water (which would, of course, increase the solids content) and to the formation of a considerable amount of colloidal aluminates.

The presence of gypsum leads to two effects in cements: (1) formation of sulfoaluminates and prevention of "flash" set, and (2) development of "false" set because of dehydration of gypsum to calcium sulfate hemihydrate when ground with clinker. "False" set is sometimes called "plaster set" and apparently proceeds by hydration of the hemihydrate to gypsum. According to some authors [7], the sulfates apparently do not affect the rate of hydration of the silicates, but Bernal, Jeffery, and Taylor [42] have proposed that gypsum prevents the formation of an aluminate gel layer on the surface of the alite. According to these authors the gel layer slows the rate of hydration. Although the details of "false" set will be examined in the future, several observations may be made on the basis of the results obtained in the present study.

False set may easily be broken up by sufficient mixing. Powers [26] has reported that the presence of "false" set influences the behavior of pastes and should be destroyed in order to obtain reproducible results. This is the reason that the mixing procedure followed in the present study was employed. The experiments on mixing procedures indicate that "false" set enhances the degree of thixotropic behavior. Nevertheless, when increasing times of mixing are used or a rest period between mixing is employed, the thixotropic structure is destroyed. This is also manifested by the appearance of antithixotropy which apparently is exhibited only in the absence of a large degree of thixotropic behavior.

The effect of alkali in cement on setting has been discussed by Steinour [7]. Alkalies in clinker have been reported by Schmidt [43] to cause the development of quick set. Alkalies in clinker have been found by Lerch [44] to accelerate the formation of sulfoaluminate and even to accelerate the hydration of the tricalcium aluminate. Cements high in alkali are reported to require higher gypsum additions.

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Discussion

A. J. Gaskin

The rheological behavior of cement pastes is influenced by so many factors that it is probably misplaced optimism to expect that clear isolation of any mechanism involved can be reached at this stage.

Ish-Shalom and Greenberg show that pastes exhibit antithixotropy at an early age if C_3A is present, and later develop thixotropic characteristics. The authors propose only the most general explanation of the main trend, attributing the thixotropy to the generation of hydration products capable of effecting cross linkages of a mechanical or possibly chemical nature, between particles.

There can be no doubt that the relative amount and nature of the colloidal hydrates will be the main factors controlling the rheology of pastes in a general sense. It may be useful, however, to give more specific consideration to certain minor factors at this juncture, in particular rheological effects possibly associated with the granular unhydrated cement particles, such as antithixotropy, and the influence of degree of flocculation on yield values and thixotropy

Antithixotropy

One possible view of "antithixotropy" is that it represents persistence of the type of grain arrangement responsible for the appearance of dilatancy, an effect common to most granular systems with an interstitial Newtonian liquid phase. The phenomenon originates in the flow mechanism described by Endersby [1] [1] as "granular structural resistance," whereby particles temporarily lock together in bridging arrays when forced into contact with one another during shear.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The intensity of the transient resistance offered by the formation of any array depends on such factors as the liquid/solids ratio, the shape of the particles, the particle size distribution, the degree of interparticle adhesion or surface friction, and the viscosity of the liquid.

If the particles are not well wetted by the liquid, or if interparticle frictional effects are reduced by adsorbed lubricating layers, the effect is weakened. Conversely, when particles are strongly cross linked or aggregated into flocs of high stability, the effect degenerates into "structural viscosity" as the relaxation time for breakdown of arrays becomes very long.

The terms "dilatancy," "false-body," and to some extent "shear-hardening" as applied to suspensions, refer to effects produced by the granular structural resistance which opposes deformation of such systems.

Classical "Osborne-Reynolds dilatancy," in which the dilation of the overall volume of the locked arrays of granules is observable during shearing, is an extreme instance of the general phenomenon, only discernible when the liquid/solids ratio is near the critical minimum required to just saturate a close-packed system of grains. Actual "close-packing" of grains is not required, the only essential being the formation of an extensive skeleton of locked arrays of particles which will hold together long enough to permit the liquid phase to flow into the internal shear cracks developed between domains of particles, and so result in drying out of the surface.

Cement pastes, ceramic oxide casting slips, and similar systems, usually have a higher liquid/solids ratio than that required for the appearance of "drying-out" on deformation, but nevertheless exhibit the more basic features of dilatancy. Surface drying is not apparent for two reasons, first, the relaxation time for destruction of arrays shortens as the liquid content of the system increases, and second, slight transient changes in the total volume of the particle arrays are not easy to detect when the surface layer of the system as a whole contains extra liquid.

There can be no fundamental objection, therefore, to the extension of the term "dilatant" to serve as a general reference to the increase in viscosity which commonly accompanies an increase in the rate of shear of granular suspensions, when it is desired to relate such a viscosity increment to the "granular structural viscosity" mechanism. Persistence of dilatant effects as shear rates are reduced then leads to the feature termed "antithixotropy".

In the broad sense dilatancy is a feature of granular systems, as distinct from colloids, and should therefore be a dominant characteristic of cement pastes and suspensions at the time of mixing, when the material can hardly be considered to be "colloidal" in any sense of the word.

Pastes show progressive change from "granular" to "colloidal" behavior as hydration products of truly colloidal type are generated within the system.

The extent to which a paste will show dilatant characteristics will depend on the ease of formation of locked arrays of particles during shear, and the extent of antithixotropy should then be governed by the persistence of such arrays, once formed, at lower rates of shear.

At first a cement paste will contain free granules and water only, and should show strongly dilatant characteristics, arrays forming readily but decaying rapidly as shear rates are reduced. The presence of the first colloidal hydrates will reduce dilatancy by restricting the mobility of the water films between the grains, but this effect, together with the growth of hydrate films on the grains, should increase the persistence of arrays (relaxation time) so leading to the appearance of antithixotropic features.

A simpler model which demonstrates the effects of increasing the relaxation time in such systems is a starch-water paste in which glycerol is progressively substituted for water, so reducing the mobility of the liquid phase [2].

A ceramic analog is found in the addition of increasing amounts of colloidal clay to a "false-bodied" granular mixture, whereby dilatant effects are suppressed in intensity but prolonged in time. If more clay is added the mass retains some "shear-hardening" characteristics which persist indefinitely even when the shear rate is reduced almost to zero.

Flocculation

In cement pastes the factor which generally appears to obscure the simple picture of a dilatant system being modified by colloidal hydration products is the degree of flocculation of both the cement particles and the hydrates.

The breakdown of floc structure on application of shear is the opposite effect, rheologically, to the formation of arrays in dilatancy. The period of recovery of structure following reduction or cessation of shearing, if long enough, results in thixotropy, and is the converse of the period of relaxation of locked arrays produced in the shearing of dilatant systems.

Initial dilatant features of pastes, such as antithixotropy, are therefore supplanted as hydration proceeds by flocculation effects either characterized by short recovery times, leading to increased yield values, or longer recovery times, giving thixotropy.

The results of Ish-Shalom and Greenberg may thus be considered as showing that normal cements containing C_3A are not strongly flocculated at periods of hydration between 15 and 45 min, but thereafter flocculation completely dominates any effects of the dilatant type. Without C_3A, pastes are well flocculated even at 15 min, and the extent to which yield values and thixotropic effects develop at later ages depends only on the proportion of colloidal material resulting from hydration.

The mechanical and chemical cross-linking factors mentioned by the authors are no doubt responsible for some of the interparticle attraction responsible for flocculation, but the impression given by the data is that some type of electrostatic flocculation is a major factor.

Recovery times appear to be short, for example, and no severe reductions in yield value or thixotropy are shown in "second cycle" data.

If the usual electrostatic considerations should therefore be applied to the cement paste system, an interesting position arises. The hydration products are known to be positively charged, and should therefore be flocculated by anions in the liquid phase, unless it is proposed that charge reversal is occurring at some critical solution concentration during the hydration process, by secondary adsorption of anions. Since this reversal is most improbable, an original reversal having occurred at a very early stage already by adsorption of calcium ions, it seems likely that the paste components remain stable, with positive charge, throughout the period under consideration, the stabilizing ions being calcium and any other cations in the solution phase.

Flocculating ions must then be either hydroxyl, or the more effective divalent anionic components of the solution, mainly sulfate ions.

The degree of flocculation will then be determined by the balance existing at any stage between positive dispersing ions such as calcium and the alkalies, and flocculating anions such as sulfate and hydroxyl.

The function of gypsum and its dehydration products may then be to supply calcium in soluble form, as far as the dispersing action of these components is concerned, although the reason for gypsum addition is primarily the need to avert the formation of hydrates of C_3A.

Once the conversion of C_3A into a sulfoaluminate phase has been accomplished, it may therefore be deduced that the sulfate ion in solution is unwelcome, as it will give rise to a high degree of flocculation, increasing the yield value and plastic viscosity of the paste and hence resulting in an unnecessarily high water requirement for standard consistency.

Reduction of sulfate concentration through extensive sulfoaluminate formation may be expected to cause a reduction in the intensity of flocculation. It would be interesting to know whether the relative delay in the appearance of thixotropy in pastes containing C_3A is connected with such a mechanism.

Again, if sulfate is replaced by a less potent flocculating ion, as in the addition of barium chloride after the initial mixing period, reduction of paste consistency should follow, rather than thickening. Conversely, addition of extra sulfate without concurrent addition of an efficient stabilizing cation, as in the addition of ammonium sulfate for example, should cause further thickening of pastes not already fully flocculated. Trivalent anions, though difficult to retain in solution in pastes, should also promote flocculation, as for instance in the addition of ammonium phosphate.

The whole question of the stiffening or dispersing effects of additions of soluble inorganic salts to pastes should, theoretically, be a matter of anionic flocculation and cationic dispersion.

The picture for organic additives is complicated by the introduction of effects due to orientation of large molecular groups during adsorption on the solid phase resulting in special types of peptization or flocculation. In some instances the stabilizing action of a cationic group can still be observed, however, as in the adsorption of cetyl-trimethyl ammonium bromide, reported by Bruere [3] to be a dispersant of cement once the first oriented layer is adsorbed and covered by a second layer in which the molecules present positive polar groups to the surrounding solution.

In practice the flocculating effects of added anions may be obscured by precipitation, or by concurrent adsorption of highly polarizable cations, but if these factors are taken into account the results seem to be in accord with the theoretical predictions which follow from the model proposed above.

In our laboratory no striking exceptions to the proposition have yet been found. If calcium adsorbed on the particles of a paste, or in the interstitial solution, is stripped out as a precipitate, flocculation becomes very intense if no other suitably adsorbed cation is introduced.

If sulfate is removed and no substitute strongly flocculating anion is introduced, the paste reverts toward the deflocculated state. The ultimate state of all pastes is of course determined by the progress of hydrolysis of the primary clinker compounds, liberating calcium as the stabilizing cation and hydroxyl as the dominant counter-ion.

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Closure

Moshe Ish-Shalom and S. A. Greenberg

Dr. Gaskin in his discussion of our paper has presented a model for the hydrating cement system to explain the flow behaviors observed. In the early stages of hydration he presumes that a paste consists of free particles in water and that as hydration proceeds the colloidal products coat the unreacted particles and flocculation occurs. The "antithixotropic" flow behavior found in fresh pastes after 15 min of hydration (fig. 1, curve A), he attributes to a system of portland cement particles dispersed in water and he states that this system should be dilatant. He has suggested also that the thixotropic properties develop in pastes as the "degree of flocculation" increases with hydration. It is of interest to compare the model proposed by Dr. Gaskin with the experimental evidence.

The authors of this article have avoided giving a detailed explanation for the flow behaviors of fresh pastes for two reasons:

1. The terminology and definitions that are used to describe the flow behaviors of relatively simple aqueous dispersions, which are stress-dependent, have not been standardized. Therefore, there is a great deal of confusion on both the colloid chemistry and rheology of dilatant and thixotropic systems in particular. The situation has also been complicated by the variety of methods used to measure the flow properties of dispersions.
2. The various physicochemical factors, which influence the flow properties of fresh pastes, are not well understood. Dr. Gaskin in the first sentence of his discussion says substantially the same thing.

A committee on communication problems in industrial rheology has been formed to establish authoritative definitions and a standard terminology for the stress-dependent flow phenomena of dispersions. This committee is sponsored by several divisions of the American Chemical Society, by the Society of Rheology, and by the American Society for Testing Materials. Up to this time the committee has issued only one article on recommended terminology [1].[1] Three basic quantities, according to the committee, are measured: (1) shear stress (S), (2) shear rate (D), and (3) time. Therefore, they recommend that the ratio S/D should be described as a function of D in each of the three broad areas of flow behavior. A constant S/D ratio is characteristic of a Newtonian system. A material which shows a decrease in the ratio S/D with increase in D is referred to as shear thinning. An increase in S/D with increase in D is given the name shear thickening. It is clear that to some investigators shear thinning and shear thickening refer to thixotropic and dilatant [2] flow behaviors, respectively.

The paper under discussion was written before the recommended terminology was available. Therefore, this terminology was not incorporated in the paper. However, in the future we shall employ these recommended terms in reporting data wherever possible. Nevertheless colloid chemists will use the words dilatant and thixotropic and they therefore must be defined. The term antithixotropic has been used by Dellyes [3] to describe the behavior of very fresh pastes (fig. 1, curve A).

The classical experiments demonstrating dilatant behavior were conducted by Reynolds [4] on sand-water mixtures. Reynolds found that an applied stress on this system caused the volume occupied by the sand to expand or dilate. Reynolds also observed an increase in rigidity of the sand-water system when the system was distorted. Working with quartz-water and starch-water systems, Freundlich and Roder [5, 6] observed an increase of "viscosity" with rate of shear. To these systems they also gave the name dilatant. On the basis of these and related experiments, it is now common [2] to ascribe the name dilatant to systems which are Newtonian at low rates of shear and are shear thickening at higher rates of shear. After an examination of the reported dilatant inorganic systems, Metzner and Whitlock [2] concluded that our information on these systems is based on a few quantitative studies and that much more research is necessary before we shall understand this behavior better.

The authors of this article would be reluctant to apply the name dilatant to cement-water systems on the basis of commonly accepted usage of the word. Curve A in figure 1 of our paper shows no indication of a Newtonian behavior except perhaps at very low rates of shear. Dilatant systems show flow curves which are concave toward the torque axis. This is not the case with cement pastes. The ratio S/D increases with *time* in this case. Antithixotropy is perhaps *related* to dilatancy but more research will be required before we understand this relationship.

Dr. Gaskin states that "At first a cement paste will contain free granules and water only, and should show strongly dilatant characteristics." Dr. Gaskin apparently defines dilatant systems as those which build up a structural array as they are sheared. We shall not argue with Dr. Gaskin's definition of dilatant behavior or his model for it, but we cannot agree that fresh cement pastes are a dispersion of free granules. Powers [7] has reported sedimentation data which demonstrate that cement-water systems are flocculated. Also with the relatively high concentration of calcium ions in the aqueous phases in pastes, flocculation would be expected [8].

In addition to cement granules in water, several investigators [9] have reported that immediately on mixing cement and water several hydration products appear. False set [10] caused by the formation of gypsum occurs only a few minutes after cement is mixed with water. In addition, hydrated calcium silicates and aluminates, calcium hydroxide, and ettringite are formed at early stages. All these species interact by physical and probably chemical bonds. Dr. Gaskin shows his awareness of this problem in the first sentence of his discussion yet he tends to ignore it in the model he proposes.

Peterfi and Freundlich [5] originally defined thixotropy as an isothermal, reversible sol-gel transformation. Freundlich later extended the definition of gel to include particles greater than 1μ in size. This behavior is attributed to the attracting and repelling forces between the particles. The application of the word thixotropic to cement pastes is not entirely consistent with the definition because the transformation is not completely reversible. Our experiments indicate at this time that only the hydrated calcium silicates form a reasonably reversible system. Many of the hydration products lead to shear-thinning behaviors, but information on their ability to completely recover their original consistency when allowed to stand will require additional research. The irreversibility in cement pastes is probably due to chemical bonds or crystalline intergrowths of the various species, which when once broken will not reform. False setting cements are an example of this behavior. False setting concretes may frequently when agitated become workable. Thus the bonds between the recrystallized gypsum particles when broken do not reform.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Apparently Dr. Gaskin misinterpreted our discussion of the bonds between the particles in fresh pastes and especially the hydrated calcium silicate particles. We believe the solids are held together primarily by attractive van der Waals forces, and we brought up the possibility of chemical bonds or crystalline intergrowths between the various species in fresh pastes. It appears that hydrated calcium silicate gels, where the particles are held together by van der Waals forces, exhibit strongly bonded structures. Dr. Gaskin refers to the word flocculation in a way quite different from the meaning we give it. We use the word to mean the reverse of dispersion or deflocculation [11]. Flocculation occurs when the attractive van der Waals forces between the particles in the paste or suspension exceed the electrostatic repulsive forces. This terminology follows that of Verwey and Overbeek [12] which obviously differs somewhat from that of Dr. Gaskin.

The assumption by Dr. Gaskin that calcium is a dispersing ion in cement pastes is not in accord with the evidence [11]. We have stated already that the evidence demonstrates that pastes form flocculated systems. Stein [13] has reported that calcium ions may reverse the negative charge of hydrated calcium silicates and thus reduce the zeta potential. These effects would lead to flocculation by calcium ions. Similarly Powers has shown [11] that calcium ions flocculate silica dispersions. No evidence has been offered to show that calcium ions by increasing the positive zeta potential can stabilize a silicate or silica sol.

In conclusion it may be said that a detailed understanding of the rheology of cement pastes will require a better knowledge of the rheology and chemistry of the colloidal and macroscopic particles in cement pastes. Research on the component systems, combinations of these systems, and on cement pastes is in progress in our laboratory.

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SESSION VI. DESTRUCTIVE PROCESSES IN CONCRETE

Paper VI-1. Chemical Reactions Involving Aggregate*

Per Bredsdorff, G. M. Idorn, Alice Kjaer, Niels Munk Plum, and Ervin Poulsen

Synopsis

This paper comprises a review of the literature concerning chemical reactions in concrete involving aggregates, with emphasis on reactions leading to deterioration because these reactions have been particularly studied as problems of concrete durability.

The first and second sections deal with different inorganic and organic impurities—or contaminations, or constituents—of aggregates. There follows a brief account of studies on the aggregate bond strength related to chemical reactions in the contact phase and a description of a rather particular case of deterioration in harbor works in Portugal. Next, a detailed review of available papers on alkali-aggregate reactions is given. The complex character of this subject is demonstrated by the discussions in different passages. The last section contains comments on some so-far unidentified so-called cement-aggregate reactions in Canada and the U.S.A.

Résumé

Cet exposé passe en revue la littérature qui traite des réactions chimiques dans le béton comprenant les agrégats, en concentrant sur les réactions qui provoquent la détérioration, parce que ces réactions ont été étudiées particulièrement sous forme de problèmes de la durabilité du béton.

Les première et deuxième sections traitent des différentes impuretés organiques et inorganiques—soit contaminations, soit constituants—des agrégats. Ces sections sont suivies d'un bref compte-rendu des études sur la résistance de la liaison ciment-agrégat relatives aux réactions chimiques dans la phase de contact, et la description d'un cas assez particulier de détérioration dans des travaux portuaires au Portugal. Puis, on fait une revue détaillée des exposés disponibles sur les réactions alcali-agrégats. Les discussions en différents passages démontrent le caractère complexe de ce suject. La dernière section contient des commentaires sur certaines réactions, au Canada et aux Etas-Unis, appelées réactions entre le ciment et l'agrégat et jusqu'à présent non-identifiées.

Zusammenfassung

Dieser Vortrag beschäftigt sich mit der Literatur der chemischen Reaktionen, die sich im Beton ereignen, an denen Zuschlagstoffe teilnehmen, und Nachdruck ist auf solche Reaktionen gelegt, die zu einer Zerstörung führen, weil doch solche Reaktionen besonders studiert worden sind als Probleme der Dauerhaftigkeit des Betons.

Das erste und zweite Kapitel beschäftigen sich mit den verschiedenen anorganischen und organischen Verunreinigungen oder Bestandteilen der Zuschlagstoffe. Danach werden die Untersuchungen über die Bindungsstärke der Zuschlagstoffe in ihrer Beziehung zu den chemischen Reaktionen in der Kontaktphase kurz besprochen, und ein besonderer Fall der Zerstörung einer Hafenkonstruktion in einem portugiesischen Hafen wird erörtert. Danach wird die vorhandene Literatur über Alkaliaggregatereaktionen besprochen. Wie kompliziert dieses Gebiet wirklich ist, ist an Hand einer Besprechung verschiedener Literaturstellen dargelegt. Das letzte Kapitel enthält Bemerkungen über einige Zementzuschlagstoff Reaktionen, die in Kanada und den Vereinigten Staaten aufgefunden und niemals näher identifiziert worden sind.

Introduction

Very different types and circumstances of reactions were in mind when the compilation of papers for the present report commenced. However, the majority of papers available dealt with alkali-aggregate reactions which apparently represent the most pronounced menace to concrete durability in rather extensive areas. It has appeared that pertinent problems in the field of alkali-aggregate reactions are still unsolved, and some questions may even be considered as unapproached, at least as judged from published works.

In many respects, therefore, the report is rather incomplete in the sense of forming a synthesis on the basis of hitherto reported investigations of the different aspects of the reactions. Moreover, the paper is mostly qualitative, because it so far has not been possible to interpret the available data adequately in quantitative models. One major problem, which in the opinion of the writers is not clarified sufficiently, is the fundamental nature of the chemical reactions between alkalies and reactive aggregates and the nature of their mechanical effects. Problems regarding a proper realization and evaluation of empirical tests is another field where still much research will be needed, and the

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"unidentified cement-aggregate reactions" is one more important question to which the clue might be hidden in the solution of the former two problems.

On the whole, the report may have developed into too much of an attempt at presenting that which is not known today about alkali-aggregate reactions, rather than being a mere compilation of existing data. It is hoped that the viewpoints brought forward in this treatment may be found useful with respect to further research. The writers also hope that the unavoidable imperfection of the paper will be eliminated by supplementary contributions from other authors.

Inorganic Impurities in Aggregates

Oxidation, hydration, and carbonation of oxide minerals in aggregates have repeatedly been said to cause troubles in concrete.

E. G. Swenson and V. Chaly [1][1] reported that magnesia as an impurity in aggregates may occasion damage by carbonation, due to a considerable volume increase and to a higher solubility of $MgCO_3$ than of the original periclase. R. F. Blanks and H. L. Kennedy [2] mentioned a concrete canal lining in California, in which pop-outs developed, because magnesia and lime in the aggregate expanded by hydration and carbonation.

Pyrite and marcasite may also expand by oxidation and hydration. They may further cause disintegration by being the sources of a development of free sulfuric acid and sulfates, which may dissolve the binding constituents of the cement paste and precipitate vulnerable substances as gypsum and ettringite. T. Hagerman and H. Roosaar [3] recommended about one percent as the upper limit for the content of the easily oxidizable sulfide minerals, especially iron pyrite.

I. Moum and I. Th. Rosenqvist [4] reported severe concrete deterioration in the Oslo region, caused by alum shales containing small amounts of pyrite and pyrrhotite. The latter mineral, easily weathered, produces an unusual kind of sulfate attack when concrete is placed in or near rock foundations of alum shales. Severe and rapid deterioration of this type has been a rather common occurrence in foundations, tunnel linings, sewers, etc., in and around the town of Oslo for a number of years. The critical limit of the content of pyrrhotite in the shale seems to be as low as about 0.01 percent, when normal portland cement is used. In recent years sulfate resistant cement with low C_3A-content has been recognized as a reliable safeguard.

In some cases, where alum shales by accident or for economic reasons have been used in the aggregates, seams of ettringite have been observed to develop as reaction rims in the adjacent paste around the alum-shale pebbles. This reaction has caused cracking and disruption, probably initiated by swelling and partial dissolution of such pebbles.

Alum shales similar to those of the Oslo region are mentioned to occur also in other countries. A detailed account of the Norwegian problems is given [5] by R. Bastiansen, I. Moum, and I. Th. Rosenqvist.

G. M. Idorn [6] reported a case of comprehensive development of pop-outs in lightweight concrete blocks made with cinder slags as aggregates and used for the inner walls in multistory flats. Petrographic examination of thin sections of the damaged concrete suggested that swelling of slag particles, presumably due to delayed reaction of pyrites in the slag, led to the development of the pop-outs. The damage was observed on plastered walls only and continued to occur during the following 10 yr on bathroom walls (humid) as well as on walls of living rooms (dry). Evidence of delayed hydration of hard-burned lime (CaO) as a deleterious factor was looked for, but was not found.

Sulfate reactions in concrete may in some regions be due to the presence of gypsum in the aggregates. The effects may be expansion, cracking, and further disintegration by alteration of the hydrous calcium aluminate and silicate with additional development of calcium aluminosulfate, etc. R. F. Blanks and H. L. Kennedy [2] suggest that the upper limit for the content of gypsum in coarse aggregate should be less than 0.25 percent by weight.

Zeolitic minerals and some clays of the montmorillonite types are subject to base exchange by which calcium ions from the cement paste are adsorbed, replacing sodium and potassium ions in the said minerals. These changes may affect potential alkali-aggregate reactions as mentioned later. However, setting and hardening of the paste may also be affected, and efflorescences may develop on surfaces. R. F. Blanks and H. L. Kennedy in their book [2] mentioned that concretes with such efflorescence and cases of deterioration in southern California were ascribed to a base exchange in zeolites.

R. E. Grim [7] mentioned that if the soil around concrete members, basements, pillars, etc., contains montmorillonite clays, a base exchange may take place between sodium from the mineral and calcium from the hardened cement paste. Grim stressed the possibility of tremendous effects on structural stability by such an exchange. A further treatment of this subject, however, is not within the scope of the present paper.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Organic Impurities in Aggregates

Different organic impurities and contaminations in aggregates are reported chemically active in concrete.

M. F. MacNaughton and J. N. Herbich, for instance [8], mentioned some rather peculiar cases of accidental air-entraining in concrete due to the presence of some organic substance in the aggregate. The substance was not detected by standard testing of the aggregates, but it was possible to isolate a nonvolatile brown crystalline solid, which possessed foaming properties when used in concrete mixtures. The air entrainment could amount to about 7 or 8 percent, but was unstable and not controllable. Aggregates of this type are said to occur frequently in Ontario, particularly in the area covered by the Laurentian shield.

Abnormal hydration of cement paste due to certain organic impurities of aggregates and sometimes causing serious decrease of strength and durability have been investigated and discussed for many years. For instance, E. G. Swenson and V. Chaly [1] characterized the following organic impurities as deleterious: soil, humus, wood particles, bark, coal, lignite, and other vegetable and animal products. The standard colorimetric test was, by the authors mentioned, regarded as effective in detection of harmful quantities of the substances, although the presence of coal or lignite could cause anomalous results.

Other authors have, according to recent research, questioned the validity of the colorimetric test.

F. S. Fulton [9] mentioned that much trouble with South African concrete structures had been traced to contamination of aggregates by sugar and that the colorimetric test had been useless.

T. Karttunen and T. Sneck [10] prepared a literature summary concerning the influence of humic sand on the strength of concrete. They found that when the quantity of organic impurities in sands is to be estimated by the colorimetric NaOH test, it is common practice not to take into account the chemical nature of the impurities. The test, therefore, is not considered reliable. Investigations of reported cases regarding the influence of humic compounds on durability suggest a marked decrease of durability now and then, whereas other authors have not observed any influence at all. Attempts to neutralize humic compounds in sands are reported in some cases to have improved the quality of the concrete, while other authors have not found any effects of such measures. Karttunen and Sneck suggested that the cement composition might be a factor influencing the effects of humic compounds. They mentioned that Forsén had observed humic substances to act as accelerators in the presence of alkalies.

Cement-Aggregate Bond Strength

Later in the present paper is mentioned a case where improvement of the bond between chert aggregate and cement paste in a concrete was believed to be due to mild alkali-aggregate reaction. K. M. Alexander [11] discussed the possibility of a similar type of reaction in a study of bond strength. In the case of an opaline aggregate, stronger bonds than with inert aggregates developed in 7 days (with low-alkali cement), whereas reactive volcanic rocks did not develop significantly better bond than inert aggregates in the same period. Incidentally, the bond strength was found to depend upon a considerable amount of other physical and mechanical factors. J. Farran [12] claimed that flint (from northern France) gave a bad bond strength. The same result was attained with mica minerals, whereas quartz performed better, and calcite and dolomite were found to adhere excellently to cement paste. The author suggested that some rearrangements of the lattice in the contact phase between aggregates and paste developed a particular type of "epitaxy". This phenomenon is generally known among metallurgists. According to C. Zwikker [13], "epitaxy" means that electrolytically deposited metals tend to adapt themselves to the lattice of the metal base, a result of the surface electrical field, and hence exhibit stresses. Farran suggested that such epitaxy would cause better adhesion in concrete with limestone or dolomite than with other rock types and also would cause pneumatically applied mortar to adhere better to limestone rocks and dolomites than to various other metamorphic and igneous rocks.

The Port Leixões Case

An extensive investigation of maritime works in Portugal, reported by M. Rocha, A. Coutinho, and A. Beja Neves [14] suggested certain chemical reactions between cement and aggregate to be a disintegrative factor. Nine harbors along the Atlantic coast were inspected, and the behavior of concrete and joint mortar in ashlar work was recorded. Chemical analyses were carried out for determining the alterations of cement paste. Rough estimates of the rock compositions of aggregates were also made, and the original mix compositions were calculated with a view to a comparison with records from manufacturing.

Rapid deterioration was found to occur in the north region only and had particularly progressed in the works of Port Leixões. All the cements applied were of national brands complying with the standard specification, but it appeared that the concrete showed durability and decay as well. Nor was the cement content found to be related to the deterioration, as in much of the bad concrete 300 or more kilos of cement per cubic meter had been used. Unsuitable grading of sand was mentioned as a possible contributory factor in causing poor workability of the fresh concrete and high permeability of the hardened concrete, thus facilitating soaking by sea water and concentration of salts by evaporation.

The severe deterioration was believed to be primarily due to certain chemical reactions between the cement and constituents of the aggregates, though under additional influence of the presence of sea water. This hypothesis was found sustained by the observation in Port Leixões, inasmuch as white exudations developed in joint mortar before it had been exposed to sea water. Likewise, some 90-ton blocks for a submarine breakwater showed cracking and exudations of a white substance through the cracks already during storage before placement in the water. However, a chemical analysis of samples of the exuded substance on some of the blocks that had been stored immersed in sea water for 1 yr proved the substance to contain only a minor amount of silica, and a negligible amount of alkalies, see table 1.

Also, in a jetty at Port de Peniche severely deteriorated blocks were found showing a pattern of deep, wide cracks. Chemical analyses of cement paste of such blocks proved the paste to be chemically unaltered and sound, and the appearance of the cracks suggested internal expansive reactions rather than superficial chemical attacks from sea water.

The fine aggregates in question consisted of about 85 percent of quartz, 14 percent of feldspar, and 1 percent of accessory mineral. Sometimes the feldspar was somewhat disintegrated. Coarse aggregates consisted of granite, occasionally with kaolinized feldspar.

Table 1. *Chemical analysis of white substance exuded through cracks in concrete blocks for a submarine breakwater in Port Leixões*

From [14]

Component	Percent
CaO	7.5
SiO_2	1.1
Al_2O_3	9.9
Fe_2O_3	3.0
MgO	27.2
SO_3	1.0
Loss at 105 °C	18.0
Loss at 500 °C	42.7
Loss on ignition	48.6

In the paper the deterioration seems ascribed to some reactivity of these rocks. The comprehensive analytical work presented seems in its entirety to offer further information about the action of sea water on readily attackable cement paste in porous mortars and concrete. Figures 1 and 2 are reproductions of two series of analyses, showing the compositions of the cement paste in deteriorated samples taken from different heights within the reach of tide and waves. The composition of the original cement is also tabulated.

The most pronounced alterations can be seen to have occurred in the range from about +0.50 to +3.00 m, where a marked decrease in CaO corresponds to an increase in MgO. Also an increase of the SO_3 content seems significant. Presumably the cause of the changes is leaching combined with precipitation of $Mg(OH)_2$ and possibly also of calciumaluminosulfate or maybe even gypsum, and the compilation of the data should be considered of interest to anyone dealing with such troublesome work as diagnosing disintegrated concrete.

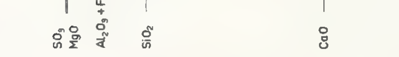


Figure 1. *Chemical analyses of cement in mortar, affected by sea water.*

Pier wall (mur d'arcades), Port Lexiões, Portugal. Alteration of cement comprises augmentation of MgO and SO_3 and a very marked decrease of CaO. From [14].

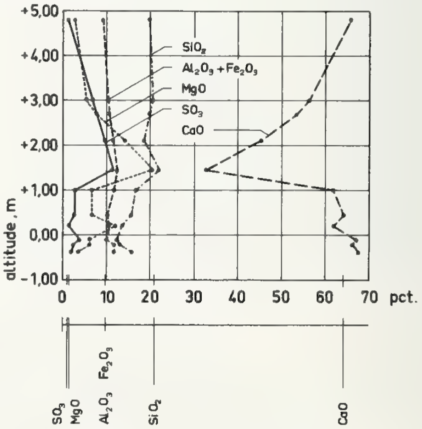


Figure 2. *Chemical analyses of cement in mortar, affected by sea water.*

Pier wall (mur continu), Port Leixões, Portugal. Alteration of cement comprises augmentation of MgO and a very marked decrease of CaO. From [14].

Alkali-Aggregate Reactions

Aggregate particles that contain or consist of silica in an amorphous or low-crystalline phase are, in concrete, attacked by alkalies and lime from the liquid phase of the cement paste. Rocks and minerals in aggregates of this type are designated alkali-reactive, and the processes are designated alkali-aggregate reactions. By these reactions is produced a solid, viscous, or liquid silica gel, holding alkali ions and calcium ions in the random network of silica molecules. By imbibition of water, the gel may either swell almost without limit, being therefore referred to as being of the *unlimited-swelling type*, or may not swell to any appreciable extent, therefore being referred to as the *limited-swelling type*.

The reactions may affect the mechanical properties of the concrete to a remarkable extent. The partial or total alteration to a gel of certain mineral components of aggregate particles represents a weakening of the physical structure of the particles and therefore also of the strength of any cross section of a concrete member containing such particles. If only limited-swelling gel is produced by the reactions, this weakening may be the only direct effect on the qualities of the concrete.

If unlimited-swell gel is produced, pressure develops, directed from the reacting particle against the ambient cement paste. This pressure may exceed the tensile strength of the mineral structure and the paste, consequently causing microfracture. Such disruption may be recognized and registered as expansion of a mortar bar, a concrete bar, or even of a structural member.

Homogeneously distributed microfracturing in a concrete mass may sometimes result in gross expansion of a structural member without any noticeable accompanying cracking, especially if reactions affect the fine fractions of aggregates only, and provided that expansions are not impeded by the static conditions.

Heterogeneously distributed microfracturing may result in overall cracking of the concrete mass, on surfaces frequently taking the character of the so-called *map-cracking* or *pattern-cracking*.

The swelling of gel in reacting aggregate particles situated in or close below a surface may cause a cone of adjacent, overlying material to fall off, forming what is commonly known as a *pop-out*. Swelling gel deposited in a void in the cement paste may likewise develop a pop-out if situated sufficiently near a surface. Exudations of gel through pores and cracks to jelly-like beads on surfaces are, besides pop-outs and cracks, a frequent evidence that alkali-aggregate reactions are going on in the concrete.

Affected structures should be considered less resistant to deleterious effects of concurrent weathering. Reacting or reacted siliceous aggregate particles that are more or less impregnated by gel may be less resistant to freezing and thawing than before reacting. Cracking may facilitate the corrosion of reinforcement and the leaching of the cement paste, and as a whole may gradually open the internal concrete structure to damaging agencies of ambient air, ground, and water. Secondary cracking, corroded reinforcement, and exudations of calcium carbonate therefore are common additional evidences of deterioration where alkali-aggregate reactions take place in exposed structures.

Reported Deterioration and Researches

U.S.A. Structural failures attributed to alkali-aggregate reaction have been reported from several states in the United States since about 1940; see figure 3, here reproduced from [15]. It is seen that after about 20 yr of research, alkali-aggregate reactions have been found to be a severe cause of deterioration over wide areas. In some of the cases freezing and thawing as well as sea-water attack is out of question, and it has been rather easy to assert that another preponderant agency of deterioration was in action. The map also shows that some major rivers apparently are "roads of infection". It seems natural that alkali-reactive minerals and rocks eroded from soils or rock formations along the upper reaches may instigate troubles along the river sides. It may, however, also be a factor that the structures in question comprise important constructions such as dams and bridges which probably will be under steady surveillance and maintenance so that deterioration is observed at an early age. Besides, an accelerating factor may be that many structures along rivers may partially or totally be exposed to a rather humid atmosphere.

Several papers by American colleagues, long since classics in any bibliography on alkali-aggregate reactions, are to be attended to later on. It appears that numerous research organizations, laboratories, and individuals have been involved in nearly every phase of the problem. Although it is impossible to mention all of them in the present paper, it seems, however, proper to list the following: State Division of Highways, California; Bureau of Reclamation, Denver, Colorado; Portland Cement Association, Chicago; Army Corps of Engineers, Waterway Experiment Station, Vicksburg; Highway Research Board, National Academy of Sciences; National Research Council; the ASTM, Committee C–9, and many others.

In recent years also, cement-aggregate reactions other than those entirely dependent on the alkalies of the cement seem to have been recognized and to have been the subject of investigation. This will be considered later.

Canada. Two cases of deterioration involving alkali-aggregate reactions have been investigated by the Division of Building Research, National Research Council, Ottawa; see, e.g., E. G. Swenson [16].

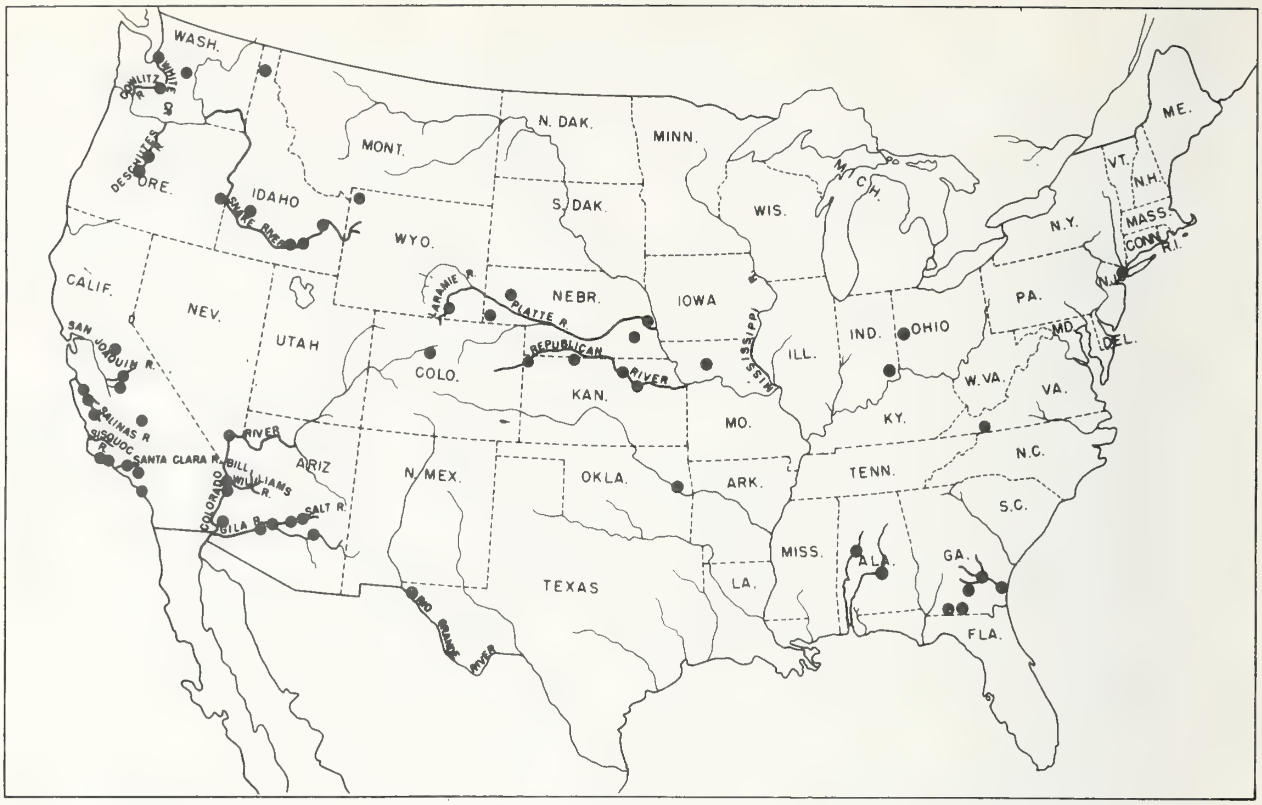


Figure 3. *Location of structures in the United States known to be affected by, and rivers known to carry, deleteriously reactive aggregate* [15].

One case comprised two sections of the deck of a bridge in eastern Canada. Troubles caused by expansion of the concrete had already been met with about 7 yr after its construction, and at the time of investigation at 25 yr, deterioration was everywhere severe. In one section almost half of the coarse aggregates were found to be phyllites, chalcedonic sandstones, and other alkali-reactive aggregates, and the concrete showed extensive evidence of alkali-aggregate reaction. In the other section only minor amounts of alkali-reactive materials (less than 1 percent) occurred in the aggregates, and evidences of alkali-aggregate reactions were not found in the concrete in spite of its considerable expansion. It was concluded that a not fully understood type of cement-aggregate reaction was going on.

The other case was encountered at Kingston, Ontario, and comprised several structures, all made with the only available local coarse aggregate which was a dolomitic limestone. Investigations showed that the troubles were due to some chemical reactions between the cement and the limestone and that the alkalies of the cement were a factor. The reactions were, however, not of the ordinary alkali-aggregate type, as siliceous mineral components were absent.

Ethiopia. S. W. Stephensen has [17] reported an alleged case of alkali-aggregate reaction in Deri Dawa, Ethiopia. A two-story, reinforced-concrete framework was found cracked to a much higher extent than could be explained by lacking reinforcement, etc. No deterioration occurred until 4 yr later, but damage then followed quickly. The aggregate was reported to contain alkali-reactive minerals. Similar deterioration was found in some other structures in the same town.

India. Cases of deterioration of field concrete due to alkali-aggregate reactions have so far not come to the knowledge of the writers. Research undertaken in recent years, e.g., by P. J. Jagus and N. S. Bawa [18] and H. L. Uppal and M. Singh [19], has shown that alkali-reactive aggregates of different types are not uncommon in India.

It is, according to B. S. Sathya Narayanswami [20], considered important at this early stage of development of the utilization of concrete to become aware of the risk of deleterious reactions that might occur in future construction. Research seems predominantly conducted by the Concrete Association of India, the Central Road Research Institute, and the National Institute of Engineering, Mysore.

Australia. No cases of structural deterioration due to alkali-aggregate reactions have so far come to the knowledge of the writers. However, in the field of research, extensive work has been carried out by A. R. Alderman, A. J. Gaskin, R. H. Jones, and H. E. Vivian, with regard to both studies of the mechanism and testing methods, in particular the mortar-bar test. Several papers have been issued by the Council for Scientific and Industrial Research since 1947 [21].

Great Britain. So far no cases of structural failure have been reported from Great Britain where damage has been due to alkali-aggregate reactions. However, the Building Research Station has carried out an extensive work now described by F. E. Jones [22, 23] and by F. E. Jones and R. D. Tarleton [24, 25, 26] in order to investigate English cement and aggregates and possible interactions of any combinations of these in mortar and cements. In short it has been found that, as a rule, cements high in alkalies are applied and that alkali-reactive aggregates do occur and often are used in some parts of England but may generally be considered not to be "expansively reactive". The research carried out also provides extensive critical data on different testing methods and procedures elaborated upon for recommended testing. Some details of the contents in the papers mentioned are to be referred to later on. Additional investigations carried out by F. E. Jones on Danish reactive aggregates, etc., are reported in [27] and a survey of durability of British reinforced concrete in buildings is given in [28].

Holland. A rather peculiar case of cracking phenomena in concrete is attributed by the late R. A. J. Bosschardt [29] to alkali-aggregate reactions. At a factory for precast concrete products some slabs were found to develop cracking when they, after some weeks' curing with subsequent drying in the factory, were exposed as stock to moist weather in free air. The cracks appeared as starlike formations on the surfaces of the slabs and were explained as developed over expanding aggregate particles. The aggregates originated from the Rhine and were found to contain siliceous rocks such as cherts and flint.

Sweden. Investigations conducted by a representative Committee on Deleterious Aggregates in Concrete have shown that deterioration of the concrete in a dam in northern Sweden was at least partly due to alkali-aggregate reactions and that some carboniferous phyllites were the alkali-reactive part of the aggregates. Quartzites and sparagmites from other aggregate sources were also found to be alkali-reactive by some of the ordinary accepted tests.

These rocks, however, in some respects did not at all show evidences of the general type of alkali-aggregate reaction. Physical factors have been suggested to play a part, but also the possibility of other cement-aggregate reactions is under investigation.

Norway. Investigations, undertaken by the Norwegian Geologic Research Institute, concerning alkali-reactivity of certain phyllites in Norwegian aggregates are said to be in progress. Results have so far not been reported.

Denmark. The first observation of field failure attributed to alkali-aggregate reactions is referred to by P. Nerenst [30]. Thereupon, in 1952–53, preliminary investigations were undertaken by the Danish National Institute of Building Research with the assistance of the F. L. Smidth Laboratories under the direction of Th. Heilmann. The work carried out demonstrated that alkali-aggregate reactions occurred in concrete all over the country. Cases of severe and rapid deterioration were found at different places, chiefly however, in coastal areas. Ordinary aggregates containing types of flint were found to be highly alkali-reactive.

These preliminary results in 1954 led to the establishment of a representative Danish Committee on Alkali Reactions in Concrete by the Danish National Institute of Building Research and the Academy of Technical Sciences (ATV).

Detection of Alkali-Aggregate Reactions

It is well known that Th. E. Stanton in 1940 for the first time stated that chemical reactions between alkalies from the cement and siliceous rocks in the aggregates were a cause of deterioration of concrete structures.

The first matter thoroughly investigated concerned a pavement in Bradley, California, which in 1938, only a little more than a year after its construction, failed by excessive expansion and cracking. Severe and rapid deterioration of concrete structures had, however, for several years been a problem in California. A bridge built in 1919–20 had shown marked deterioration already in 1923. The concrete walls of a school built in 1931 were severely cracked in 1934. This was also the case with seawalls, etc. C. W. Beardsley, C. M. Wakeman, and P. S. Wright mention [31] that a viaduct in Los Angeles constructed in 1931 was in distress in 1940. With regard to many of these structures, preliminary and rather intensive investigations had been made. Stanton says [32] about the results thereof:

"In general, the number of opinions expressed equaled the number of reports made. The causes of failure advanced by the different investigators were: the sand; unsound cement; excess water; extreme variations in temperature; faulty curing; faulty concrete design; variable coefficient of expansion between different parts (including reinforcing steel); electrolysis; overstressing of underdesign; and rusting of anchor bolts, reinforcing steel, iron pipes, washers, etc."

Stanton also says that:

"The solution of the problem was complicated by the fact that, although without exception cracking of the nature described was noted only when local fine aggregate had been used, there were numerous instances where the apparently same local aggregate performed in an entirely normal and satisfactory manner."

In the Bradley pavement two different local sands had been used in alternate sections, and distress occurred in the sections only with one of the sands (Oro Fino). However, in structures made with low-alkali cements this specific sand had caused no deterioration. The sand was found to consist of 90–95 percent of chemically inactive rock types and minerals, comprising granites, feldspars, etc., and about 5–10 percent of siliceous rocks comprising opaline limestones, opaline shales, and some cherts reported to contain opal and chalcedony.

By means of mortar-bar experiments and petrographic examinations it was proved that the siliceous rocks were the reactive components, and by further studies, including elaboration of testing methods, Stanton very soon arrived at the following conclusions:

1. Deterioration was due to some siliceous rocks in the aggregate reacting with alkalies in the cement. Alkali-silica gel was produced by the reaction.
2. The mortar-bar test made it possible to reproduce the reactions and their mechanical disruptive effects—expansion and cracking—and thus to predict the behavior of the particular aggregates.
3. Decisive factors for the reactions were:

Alkali-content of the cement. No deleterious reactions would occur with cements low in alkalies, i.e., less than 0.60 percent of equivalent Na_2O.

The amount of reactive materials in the aggregate. Expansion would increase with increasing amounts of reactive material up to a certain point (the "pessimum" proportion) whereafter expansion would decrease with still increasing amounts.

The particle size of reactive materials in the aggregates. Fine grinding of a reactive material would cause decrease of expansion. However, coarse reactive aggregates might also cause little or no expansion compared with the same material in the sand fractions.

Surveys of Structural Failures

Intensive investigations of structures and aggregates were carried out all over the United States of America during the years following Stanton's inventory studies [33]. Table 2 represents a rough summary of a survey compiled by F. E. Jones [22] from different American reports.

The deterioration referred to in this table comprised map-cracking, spalling, off-setting, etc., and in some cases even considerable structural expansions have been measured.

Aggregates from the structures were also investigated and the following common rock types found to be suspiciously reactive: opaline and chalcedonic cherts and shales, siliceous limestones and dolomites, andesites, rhyolites, glassy acid volcanics, and phyllites. In many cases mortar-bar tests with these aggregates and high-alkali cements duplicated the cracking and expansion in the structures.

TABLE 2. *Survey of U.S.A. structures reported deteriorated because of alkali-aggregate reactions*

The table is prepared on the basis of [22]

Structures		Year of construction	Severe deterioration noted	Age
Type	State			
				yr
Dams	Calif.	1938	1940	2
	Calif.	1937–1938	1940–1941	2–4
	Oreg.	1932	1943	11
	Idaho	1925	1940	15
	Ark., Nebr.	----------	----------	8
Bridges	Kans.	1934	1942	8
Roads	Calif.[a]	1927	1932	5
	Wash.	1930–1931	1939	8–9
	Nebr.	1931	1932	1
	Calif.	1932	1941	9
Buildings	Va.	1912	1922, 1929	10, 17
	Kans.	1938	1940, 1942	2, 4
	Idaho	1934	1942	8

[a] From [33].

In all of the cases where the alkali content of the cement is reported, the content is stated to have been higher than 0.6 percent, and in some of them up to 1.44 percent, equivalent Na_2O, while a considerable number of comparable structures, cast with low-alkali cements, are reported to have shown excellent durability.

Recently a renewed, extensive survey of structural failures in the United States Army has been reported by the Highway Research Board [31] on the basis of a questionnaire which was circulated in 1953. A concentration of the data is given in table 3. Reported cases both of alkali-aggregate reaction and cement-aggregate reaction are represented, and also represented are the ages of the structures in question at which deterioration has been discernible. It should be mentioned that negative replies were obtained from 19 States as to the occurrence of field failures due to the men-

TABLE 3. *Survey of structural failures due to alkali-aggregate reactions and unidentified cement-aggregate reactions in the U.S.A.*

Compiled from a survey reported in [31] by the Highway Research Board

State	Records of occurring		Age of structure
	Alkali-aggregate reactions	Cement-aggregate reactions	
			yr
Ala.	+	+	4–8
Ariz.	+		2
Calif.	+		1–5
Fla.	+		–
Ga.	+		6
Idaho	+	+	2
Ind.		+	12–20
Kans.		+	7
Ky.		+	–
Miss.	?	?	3–10
Nebr.	+	+	5
N.J.		+	4
Oreg.	+	+	5–10
R.I.		?	1
Tenn.		?	5
Utah	+	+	2
Va.	+		–

tioned agencies. Twelve States apparently did not reply to the questionnaire.

Very interesting statements appear in the comments to this survey. B. Tremper [34] mentions that as regards the western United States, three States reported failures ascribed to the cement-aggregate reaction. In Arizona, the alkali content of the cements has been limited to below 0.60 percent for the last 10 yrs, and troubles have so far not been encountered in structures from this period. In California, low-alkali cements are mentioned as the sole corrective measure since about 1943. Although in many cases highly reactive aggregates have been used as judged from comprehensive field surveys, results have been quite satisfactory.

C. W. Beardsley, C. M. Wakeman, and P. S. Wright [35] report for the Los Angeles area: Many examples of alkali-aggregate reaction occur. Restrictions for the use of potentially reactive aggregates and low-alkali cements are generally prescribed.

W. E. Gibson [36] reports for the central United States: Only two States that replied observed alkali-aggregate reaction, and two others observed cement-aggregate reactions. These reactions were particularly severe in Kimball, Nebraska, and in St. Francis, Kansas, in some cases where low-alkali cements were used. (See further in a later section.)

D. O. Woolf [37] reports for the eastern United States: Besides clear-cut cases of alkali-aggregate reaction, failures due to unsound cement, i.e., extremely high magnesia content, are also mentioned. With reactive aggregates the specification of low-alkali cement has proved a promising safeguard. However, joint cracking is observed in recent structures prepared with low-alkali cement.

In Denmark extensive field inspections have been reported from 1914, 1924 to 1927, 1952, 1954, and 1955, respectively. The first three concerned concrete of coastal structures. The fourth is a general survey inspection, a preparation for a detailed investigation.

The 1914 survey was carried out by A. Poulsen, covering concrete in coastal and maritime structures on the west coast of Jutland dating back to 1870. Much concrete made with ordinary portland cement was found to disintegrate rapidly after showing white exudations and cracking. The deterioration was attributed to the action of the sulfates in the sea water. Poulsen in 1910 invented a pozzolanic cement manufactured by grinding a Danish diatomaceous earth, "moler", together with ordinary portland cement.

On the basis of big-scale field experience and laboratory experimental work, Poulsen claimed that the use of pozzolanic cements increased the durability by inhibiting the suggested deleterious effect of calcium aluminosulfate.

In the years 1924 to 1927 a renewed field inspection of the West Coast concrete was carried out by I. K. Danø, who found wide variations of durability for both concrete with ordinary portland cement and concrete with moler cement. As a rule, however, ordinary portland cement was found to be less satisfactory. With the use of this cement, map-cracking and white exudations were typical evidences of deterioration, while surface scaling and early abrasion was attributed to the moler cement.

Both investigations are dealt with by G. M. Idorn [38] together with a renewed inspection carried out by this author in 1952. The latter inspection also covered a great deal of the concrete recorded in the two previous investigations, proving for it a considerable lifetime, i.e., a good durability. As a whole, this survey inspection corroborated the results of the previous investigations. However, the moler cement could not, to such an extent as earlier stated, be considered a sufficient protective measure against the rapid disintegration that was found to be a common phenomenon. Further studies confirmed the suggestion that the primary cause of deterioration was alkali-aggregate reaction. It appears from these studies that A. Poulsen in 1910, by inventing the pozzolanic moler cement, actually did find a a corrective measure against alkali-aggregate reactions, though he believed he was fighting the action of sulfates.

A survey inspection of Danish structures was carried out by G. M. Idorn in 1954–55 on behalf of the Danish Committee on Alkali Reactions in Concrete. The condition of some 400 structures was briefly surveyed and recorded during visits, and they were classified in six groups ranging from quite undamaged (0) to progressed, overall deterioration (5). Also the typical evidences of distress (cracking, pop-outs, gel exudations, etc.), if any, were recorded. The inspections included a good many railroad over- and under-passes; bridges across rivers, sounds, and inlets; harbor structures, etc., while pavements and buildings were little represented.

Table 4 summarizes the recorded behavior of the structures, except as to ages of the concrete. However, since few structures were older than about 25 yr, a considerable number were quite new, and as a few old ones had been subject to a general repair prior to the inspection, the classification seems to indicate that durability of structures of the categories concerned might be a prolific field of research.

Table 4. *Classification of conditions of selected concrete structures in Denmark based on survey inspections 1954–1955*

Extent of deterioration	Classification	
	Number	Percent
0	112	26
1	130	30
2	62	15
3	61	14
4	48	11
5	18	4
Total	431	100

The recorded structural behavior was also plotted against the exposure conditions, very roughly characterized as:

1. Inland location, not directly exposed to water (e.g., railroad over- and underpasses, etc.)
2. Inland location, exposed to water (e.g., bridges across streams, etc.)
3. Coastal conditions, exposed to sea water (e.g., bridges across sounds and inlets, piers, groins, etc.)

TABLE 5. *Classification of conditions of 431 selected concrete structures in Denmark based on survey inspections 1954–1955*

Behavior of structure plotted against exposure conditions, divided in the categories: Inland, no water; Inland, water; Coastal

Extent of deterioration	Classification			Total [a]
	Inland, no water	Inland water	Coastal	
	%	%	%	%
0	23	35	17	26
1	31	37	7	30
2	15	12	20	15
3	14	12	17	14
4	14	3	17	11
5	3	1	22	4
Total	100	100	100	100
Distribution according to classification	62	28	10	100

[a] From table 4.

Table 5 shows the analysis of the data. It appears that the two inland exposures seem to be of like severity (maybe because the climate in Denmark is rather humid), and they seem to be of less severity than coastal exposures. This difference may, however, not necessarily be due to the action of salts delivering alkalies or sulfates to the disintegrative reactions. The mere physical factors might also cause a more rapid weathering at the coast than in the inland areas.

Field evidences of disintegration leading to detailed studies undertaken in 1955 have been discussed by G. M. Idorn [39] and elsewhere. A list of the structures dealt with is presented in table 6. According to this survey and those previously presented, it appears that alkali-aggregate reactions may often result in an extremely progessive deterioration which necessitates extensive repairs much earlier than required by ordinary weathering.

The Danish surveys tend to show that coastal exposure may be an accelerating factor by weathering as such and by alkali-aggregate reactions in particular. These problems seem to be a promising field for further research.

At the Danish inspections, the observer was puzzled by the fact that amongst a number of quite unaffected concrete structures examples of typical and severe deterioration, obviously involving alkali-aggregate reactions, often were located within the same area. In this connection it seems relevant to point out that it was then a well-known fact that the alkali content of Danish cements varied comparatively little, and also that a difference in exposure, in cases where deteriorated as well as sound structures were mingled, was improbable.

TABLE 6. *Survey of structures dealt with by the detailed investigation 1955, conducted by the Danish Committee on Alkali Reactions in Concrete*

See G. M. Idorn [39]

Structure		Exposure		Year of construction	Severe deterioration recorded	Age
Type	Part of country	Coastal	Inland			
Bridge	Jutland	X		1939	1951	12
Do	do	X		1938	1951	13
Underpass	do		X	1942	1954	12
Do	do		X	1920	1954	[a] (34)
Pier	Funen	X		About 1930	1954	[a] 24
Sea wall	Sealand	X		1943–1947	1952	9–5
Building	Jutland		X	1947	1954	7
Do	Sealand		X	1951	1954	3
Basement	do		X	1953	1954	1
Do	do		X	1951	1954	[b] (3)

[a] Probably severely affected much earlier.
[b] Alkali-aggregate reactions not proved a decisive factor.

The American and the Danish surveys seem to disagree in that in the United States of America deleterious alkali-aggregate reactions in pavements are common and in buildings not unusual, while in Denmark pavements have so far not been reported in distress and buildings only exceptionally.

The mortar-bar test (see below) is widely accepted as an accelerated imitation of the reactions that may be expected in a concrete structure. However, the above-reported rates of deterioration seem to show that the test in many cases is not much accelerated. In other words, considering it a scale-model test, the time factor may be nearly without reduction.

Examination, Testing, and Inspection Methods

From the above it appears that the necessity of *examination* of cements and aggregates, of *testing* of these materials combined in mortars or concrete, and of a comparative *inspection* of concrete structures and concrete samples was early experienced. Table 7 is an attempt to outline the different categories of research gradually applied to these problems, introduced, elaborated, or abandoned during the first 10–15 yrs of work.

The division chosen is intended to reflect the principle that firstly it should be examined whether the components of concrete—cement, water, aggregates—contain the reactants of alkali-aggregate reactions. In this way a potential, chemically based reactivity could be either confirmed or found not existing. Every possible mechanical effect, however, representing the deleteriousness of the reactions, could not be predicted from the chemical conditions alone. Testing of potentially reactive materials, therefore, suggested concurrent measurements of mechanical effects, i.e., expansion resulting from internal disruption of mortar and

TABLE 7. *Survey of methods applied in research on alkali-aggregate reactions*

Category of treatment	Object of treatment	Method	Specification
Examination	Cement	Determination of alkali-content	Ordinary chemical analysis or flame-photometry.
	Water	Determination of alkali-content	Chemical analysis.
	Aggregates	Description of geological characteristics.	
		Petrographic analysis	Determination of rock composition and of mineral composition of rocks.
		Float separation with heavy liquids	Possible aid for petrographic analysis.
		Fluorescence examination	Recording of presence of opaline silica.
		Etching test	Recording of chemical reactivity to alkalies.
		Gel pat test	Recording of chemical reactivity to alkalies (development of alkali-silica gel).
		Quick-chemical test	Recording of chemical reactivity to alkalies (determination of solubility in alkaline solution).
Testing	Mortar (cement plus fine aggregates plus water).	Mortar-bar test Measurements of: Expansion Tensile strength Modulus of elasticity Observation of: Warping Cracking Gel exudations Internal disruption	Determination of mechanical effects of reactions.
	Concrete (cement plus fine and coarse aggregates plus water).	Concrete-bar test Measurements of: Expansion Tensile strength Modulus of elasticity	Determination of mechanical effects of reactions.
		Observation of: Warping Cracking Pop-outs Gel-exudations Internal structural disruption	Investigation of origin of mechanical effects.
		Glass-jar test	Recording of enlargements.
Inspection	Concrete structures	Field inspection	Recording of field service, symptoms of deterioration, cost of maintenance, etc.
		Supplementary laboratory investigation	Examination of concrete samples.

concrete. The application of these tests for prediction of structural behavior subsequently necessitated an ascertainment of reliable model laws, which have been studied by comparative inspections and investigations of concrete structures and test specimens. Laboratory examination, chiefly by petrographic methods, has proved to be a necessary part of such studies.

Cements

An alkali content of 0.6 percent of equivalent Na_2O was at an early stage accepted in the United States of America as an upper limit for cement used in combination with reactive aggregates. Cements considered to meet this requirement were generally termed low-alkali cement.

The fixation of the above-mentioned critical limit naturally focused attention on the previously neglected subject of the alkali contents of different brands of cement. It appeared that not only was there a wide variation in alkali contents between different brands but also that the same brand might exhibit great variations during a longer period. Examples from the literature are given below.

Analyses of about 60 American cements are given by A. D. Conrow [40]. The absolute maximum found was about 1.2 percent equivalent Na_2O and the minimum about 0.2 percent.

A. R. Alderman, A. J. Gaskin, R. H. Jones, and H. E. Vivian in 1947 [41] reported alkali contents of 16 different Australian cements showing a range from 0.12 percent to 1.09 percent equivalent Na_2O. These determinations were part of preparatory investigations on alkali-aggregate reactions.

F. E. Jones [23] compiled data on British cement from routine analyses carried out since 1928 by the Building Research Station. These data have been utilized for the graphs, figure 4, for the brands A, B, C, D (ordinary portland cement) and E, F, G, H (rapid-hardening portland cement).

The cumulative-frequency polygons for the distribution of the equivalent Na_2O (percent) are shown, and from these, as regards the brands A, B, and E, may be read:

1. The percent of analyses falling below 0.6 percent of equivalent Na_2O.
2. The mean value of equivalent Na_2O percent.
3. The approximate standard deviation.

E. V. Meyer [42] gives the determinations of alkali content in ordinary portland cement produced by one of the factories in Denmark during the years 1949–1956. A treatment of these data shows that the mean for the whole period was 0.70 percent of equivalent Na_2O, with a slight decreasing tendency for the last few years. The standard deviation is found to be 0.09 percent of equivalent Na_2O and the coefficient of variation is 13 percent. It also appears that about 15 percent of the production has had a monthly mean less than 0.60 percent of equivalent Na_2O. It is mentioned too that variations are smaller over more limited periods. Eight tests on one day are for instance reported to give a mean of 0.70 percent of equivalent Na_2O, with a standard deviation of 0.02 to 0.04 percent of equivalent Na_2O and a coefficient of variation of about 5 percent.

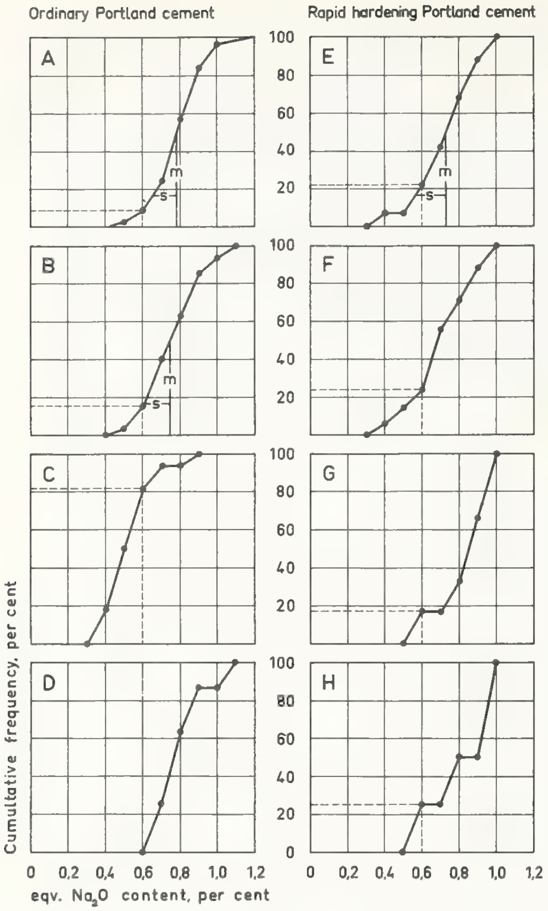


FIGURE 4. *Cumulative frequency polygons of equivalent* Na$_2$O *content of 8 British cements.*

The graphs are compiled from F. E. Jones [23].

For the 96 Danish analyses, results of monthly equivalent Na$_2$O contents during the years 1949–56, the cumulated frequency curve is outlined on probability paper in figure 5.

P. J. Jagus and N. S. Bawa [18] reported analyses of alkalies in 26 Indian cements. As the examination was preparatory, only one sample from each cement factory was analyzed. Results showed a minimum and maximum total equivalent Na$_2$O of 0.15 and 0.99 percent, respectively. Eleven out of 26 cements had total equivalent Na$_2$O higher than 0.60 percent.

From other countries the alkali contents of national brands of cement have been reported only exceptionally, and most of the available data ought to be supplemented before a critical treatment seems motivated.

The above examples suggest that many cements have average alkali contents considerably above the critical limit of 0.6 percent of equivalent Na$_2$O. The great variations observed within the same brand suggest the suspicion that some cements, considered to be of the low-alkali type, occasionally may have alkali contents above the critical limit. This view was put forward by W. C. Hanna in 1948 during the discussion of a paper by Stanton [43].

By suitable arrangements it may be possible for the producer or consumer of low-alkali cement to control the alkali content in such a way that the critical value of 0.6 percent is not exceeded.

However, the validity of the 0.6-percent limit as a general safeguard could be questioned on the basis of observations made by various authors. Th. E. Stanton already in 1943 [44] mentioned that "in any adversely reactive combination there is a markedly greater expansion of a 1:2 mortar than a 1:3 and usually a greater expansion of a 1:1 than a 1:2. However, with some highly

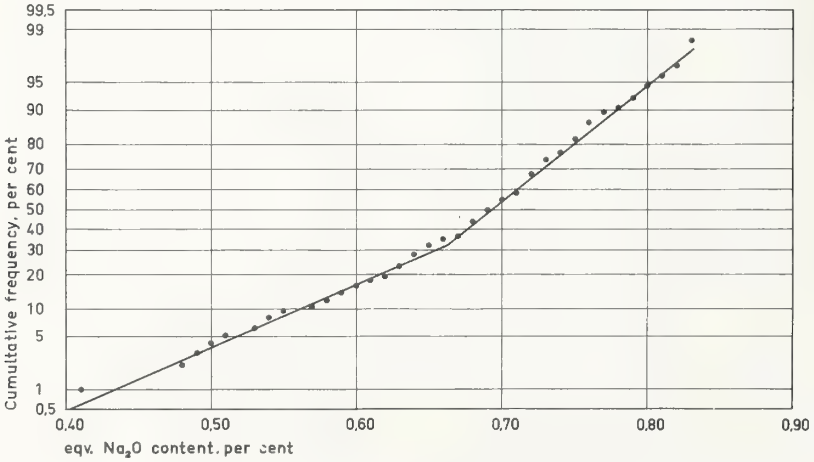


FIGURE 5. *Fractile diagram of 96 monthly averages of equivalent* Na$_2$O *content of Danish portland cement for the years 1949–56.*

The averages are plotted on normal probability paper, and it will be observed that they exhibit a marked deviation from the normal distribution.

reactive combinations the ultimate expansion appears greater with the 1:2 than the 1:1 mix". It is also mentioned that a low-alkali cement may "become quite active in mortars of equal proportions of cement and reactive fine aggregate". Consequently Stanton draws the conclusion not to use cement contents higher than 1:2 for routine testing.

Also D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45] emphasize both the alkali content of the cement and the cement content of the concrete or mortar. They state, however, that "so far no deterioration of field concrete due to cement-aggregate reactions is known to have occurred where low-alkali cements were used".

A. D. Conrow, in the discussion of a paper by W. C. Hanna [46] in 1947, reported destructive expansion in mortar bars prepared with cements as low as 0.09 percent of equivalent Na_2O, and accordingly questioned the validity of low-alkali cements as a preventive measure.

D. O. Woolf in 1948 [47] mentions that "apparently the controlling factor is not the total amount of alkali in the cement, but is the availability of the alkali for the chemical reaction". The concept of availability is discussed in the present paper in the section on mechanism of reaction.

In 1952 D. O. Woolf [48] reported the analysis of a number of mortar-bar tests made with crushed opal as the reactive component of aggregates and cements ranging from 0.22 percent to 0.99 percent of equivalent Na_2O. This investigation proved that: "Low-alkali cement used with aggregate containing a small amount of reactive material may result in objectionable expansion, while the same cement with aggregate containing a relatively large amount of reactive material may have little if any reaction". Appreciable expansion was found with cements of as little as 0.22 percent of equivalent Na_2O, when sufficently small amounts of reactive aggregates were used. Woolf mentions that similar results were reported in 1951 by C. E. S. Davis [49].

Ervin Poulsen [50] presented a statistical analysis of Woolf's test results. From this paper the mapping of expansion levels corresponding to different combinations of the percent of reactive materials in aggregate and the percent of equivalent Na_2O in cement is reproduced in figure 6. Attention should be paid to the fact that the iso-expansion curves in figure 6 are the outcome of fitting an analytical expression to Woolf's data, and the fitting is not altogether satisfactory. It will be observed that the magnitude of the expansion depends not only on the absolute value of percent equivalent Na_2O, but also on the ratio between percent equivalent Na_2O and percent reactive materials.

In view of the observations reviewed above, it may be concluded that a lowering of the limit for the alkali content of low-alkali cements will reduce the risk of dangerous expansion when reactive materials are used.

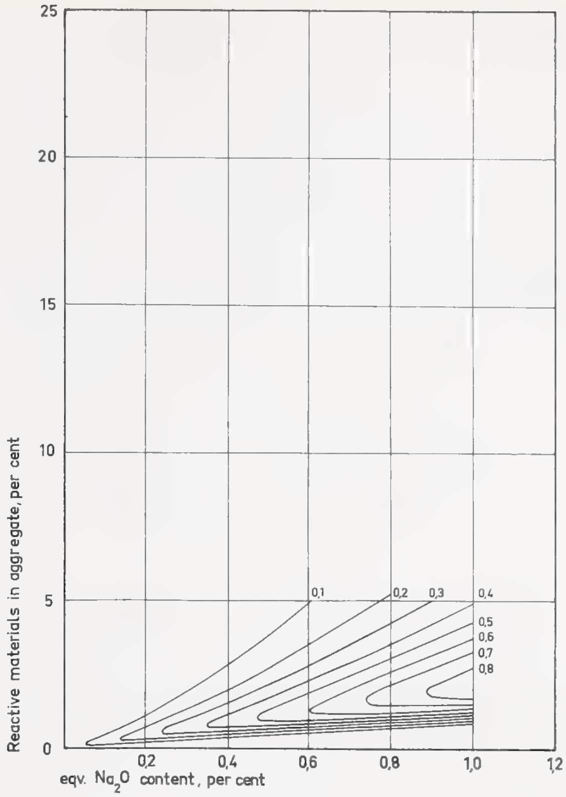


FIGURE 6. *Expansion of mortar-bars in relation to reactive material and alkali content of cement (data from D. O. Woolf).*

Each solid curve shows combinations of reactive material and alkali which give equal expansion measured in percent. Reproduced from [50].

It should be added that in cases where alkalies may be contained in the mixing water, the aggregate or the surroundings of the concrete, special precautions, besides the use of low-alkali cements, are called for.

Water

Only limited attention has originally been paid to the fact that mixing water in the case of sea water or alkaline ground water could be a possible supplementary source of alkalies in concrete.

O. J. Porter mentioned in 1942 [33] the possibility of reactions with low-alkali cements, "where the soil, water, or aggregate contains water-soluble salts of sodium or potassium". In the same paper L. C. Meder reported that addition of slight amounts of NaCl to mortar bars cast with reactive aggregates and low-alkali cements caused excessive expansions.

R. F. Blanks and H. S. Meissner in 1946 [51] and H. E. Vivian in 1950 [52] reported mortar-bar studies proving that addition of alkalies—as NaOH—might cause an increase of expansion dependent, however, on the amount of reactive aggregate, etc., i.e., in aggreement with a statement of D. O. Woolf [48] as regards the alkali-opal ratio being a controlling factor.

G. M. Idorn [53] tabulated the potential supply of alkalies to concrete by using as mixing water either sea water, brackish water, or salt ground water (of recorded Danish types). The calculations appear in table 8.

So far such results have not caused any prescriptions of analyses of mixing water, nor of avoidance of contaminated water, nor special care in placing concrete in alkali soils or sea water.

Table 8. *Supply to concrete of alkalies from mixing water, when different water types and different w/c ratios are used.*

Type of water	Sodium milligrams/liter	Supply to alkalies in cement Na_2O, percent by weight		
		w/c=0.5	w/c=0.7	w/c=1.0
Sea water	12,000	0.8	1.1	1.6
Brackish water	4,000	0.3	0.4	0.5
Salt ground water	250–1,500	max. 0.15	max. 0.15	max. 0.20

Aggregates

Earlier, it is mentioned that Stanton in 1940 found opal, opaline shale, and some cherts to be alkali-reactive. Already in 1940 the alkali reactivity of some andesitic rocks was set forth by H. S. Meissner [54] and by B. Tremper [55].

These identifications of the alkali-reactive constituents of the aggregates suggested that the actual reactive substances were those consisting of silica in either an amorphous (opal, volcanic glass) or a low-crystalline phase (cherts).

Opal, which may be characterized as a solidified, water-containing gel, occurs in various manners. It may be found as a distinct mineral, e.g., in basaltic lava or in shale, etc., or as a coating substance on pebbles of sedimentary rock deposits. It is then hard, though it is porous and of a low specific weight. It also occurs as an interstitial material in limestone formations, sometimes together with flint and cherts. In these conditions opal may form part of extremely light, porous rocks which over widespread areas are common in moraines and in beach and river deposits.

Volcanic glass may be considered an undercooled melt which, in order to be alkali reactive, must be rich in silica and may accordingly occur as interstitial substance in acid volcanic rocks. Also basic lavas may be found alkali reactive, when partly crystallized, because the remaining glass will be more acid than original glass prior to crystallization. Thus basalts also may sometimes be potentially alkali reactive, and reactivity has recently been confirmed by some tests according to the quick chemical method carried out in Denmark on basalts from Greenland. Both opal and glass are metastable under normal geological conditions compared with the regularly crystallized phase of silica in quartz. Therefore, incipient crystallization—devitrification—may be found in glasses. Likewise, during geological ages crystallization tends to proceed in opaline silica in limestone, etc., thus developing cryptocrystalline phases appearing as flint or chalcedony. Similar tendencies of crystallization may be met with in opal occurring in vacuoles or veins in basalts.

This classification of alkali-reactive minerals is believed to cover the majority of reactive silica materials in concrete aggregates, and only some exceptions need particular comments.

The minerals tridymite and cristobalite, which are crystalline modifications of silica, have been reported alkali reactive, see, e.g., F. E. Jones [22]. T. M. Kelly, L. Schumann, and F. B. Hornibrook [56] reported expansion of mortar bars where only tridymite (from silica bricks) could be the reactive component. However, both minerals are rare and of little importance in concrete aggregates, but they are of interest in the system of silica minerals, both being metastable phases of crystalline silica at ordinary temperatures. Their reactivity may therefore be regarded as related to the metastability.

Sandstones and quartzites have been claimed reactive by some authors. In sandstones the binding matrix may be amorphous or cryptocrystalline silica and therefore reactive. Orthoquartzites are quartzose sandstones with sedimentary megacrystalline quartz as the binding matrix. Metaquartzites originate from metamorphosis of such sandstones and also contain only megacrystalline quartz. Reactivity of these rocks is not a priori to be expected.

B. Mather, however, in 1951 [57] reported exudations of gel in highly fractured quartzite pebbles in deteriorated concrete, and L. S. Brown in 1955 [58] mentioned a quartzitelike aggregate, reported as strained quartz, to have caused distress.

P. J. Jagus and N. S. Bawa [18] reported significant expansions of mortar bars with quartzite as the reactive constituent of aggregate.

Having discussed quartzite and strained quartz, we are approaching the perfect order of crystallization of silica represented by pure, megacrystalline quartz which, however, is considered quite inert in the general sense of alkali reactivity and is, therefore, used as blind material in standard tests of suspicious aggregates.

Regarding an artificial silica material, we have in Pyrex-brand glass an undercooled, rather pure silica melt, i.e., an amorphous phase which inevitably is alkali reactive and therefore is commonly used as a standard reactive material for the purpose of comparison.

A survey of the described family of silica minerals is given in table 9. Also mentioned in this table are those common rocks that contain silica and may occur in concrete aggregates, causing these to be alkali reactive. Fortunately, it has repeatedly been found that the widespread minerals of the silicate group are not reactive. This fact and the inertness of quartz places all the igneous and most of the metamorphic rock types among the alkali-inactive aggregates.

Table 9. *Silica minerals and rocks*

Reactive substance	Physical structure	Chemical formula	Rock types
Opal	Amorphous	$SiO_2 \cdot nH_2O$	Concretions in basalts and other lavas. Opaline limestones. Opaline cherts. Opaline shales. Different coated rocks.
Silica glass	Amorphous	SiO_2 [a]	Rhyolitic, andesitic and other acid lavas and their tuffs, containing glass matrix. Synthetic glass (Pyrex glass).
Chalcedony	Crypto- to micro-crystalline.	SiO_2	Siliceous limestones. Flints. Cherts. Sandstones, with chalcedonic matrix.
Cristobalite tridymite.	Crystalline	SiO_2	Ceramics.
Quartz [b]	Crystalline	SiO_2	Quartzites. Sands. Sandstones. Igneous and metamorphic, acid rocks.

[a] With minor contaminations of other oxides etc.
[b] Reactive in some quartzites and when strained, microfractured, etc.

A possible, though questionable, exception is one or more of the mica minerals. R. W. Carlson in a contribution to a discussion of [33] mentioned that 5 percent of muscovite mica in a sand caused excessive expansion of mortar bars with high-alkali cement. This quite unique statement may possibly be supported by some evidences of reactivity of phyllites which can be characterized as a metamorphic, mica-rich, argillaceous shale.

R. J. Holden already in 1935 attributed deterioration at Buck Hydroelectric Plant, Virginia, to a chemical reaction between cement and phyllites in the coarse aggregate. The reaction was later found to be alkali-aggregate reaction and the reactive mineral constituent was assumed to be a "hydromica", see, e.g., D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45]. E. G. Swenson [16] referred to a case of alkali-aggregate reaction in a bridge in Canada and mentioned phyllites as the reactive rock in coarse aggregate, without discussing the reactivity of the components of the phyllite.

Recent observations pertaining to cases of deterioration in Sweden (see T. Hagerman [59], indicate deleterious reactivity of phyllites also without so far having disclosed the reactive constituents. In the opinion of the writers these may be microcrystalline quartz present in the rock just as well as hydromica. Likewise, the above case mentioned by Carlson may possibly cover processes other than the alkali-aggregate reaction, maybe even purely physical processes. Hence, alkali reactivity probably still should be considered limited to the different phases of silica minerals with regular megascopic crystallized quartz as the only safe exception.

Some minerals of the zeolite and montmorillonite groups are capable of releasing alkalies by cation exchange. Zeolites may be found in vacuoles in basaltic rocks (which also may contain some volcanic glass and opal), and montmorillonite occurring in some clays may be met with as a contamination of aggregates. Actual examples of deleterious alkali-aggregate reaction dependent on alkalies from these sources are not known to the writers.

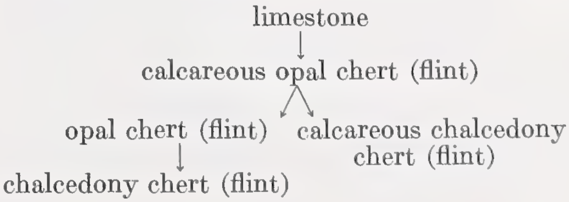
There seem to be widely different opinions with regard to the mineralogical composition and structure of flint and chert types and with regard to the cause of alkali reactivity of chalcedony. J. D. H. Donnay [60] found, by means of specific-weight determinations, that chalcedony is a low modification of quartz containing interstitial opal. B. Mather [61, 62] basing his investigation on optical measurements, agreed with this conclusion and suggested that the potential reactivity of chalcedony is due to the content of interstitial opal. In agreement with these authors is ASTM designation C 294–56 T, which states: "It (chalcedony) is now generally believed to be composed of a submicroscopic mixture of fibrous quartz with a smaller but variable amount of opal".

H. G. Midgley opposed the above hypothesis on the composition of chalcedony. By petrography, X-ray photogrammetry, and measurements of specific surface it was found that chalcedony consists of a network of microcrystalline quartz with numerous micropores, but does not contain any opal. C. R. Pelto [64] mentions that this "quartz-with-holes theory" may explain many unsolved problems regarding chalcedony, but not, for instance, the solubility and the chemical reactivity of the mineral.

In Denmark, the problems concerning the composition, structure, and properties of flint have been taken into consideration during the investigations conducted by the Danish Committee on Alkali Reactions in Concrete. Research work on the geology and petrography of flint has been carried out by A. Berthelsen [65], H. Gry and B. Søndergaard [66], and F. E. Jones and H. G. Midgley [27]. X-ray photogrammetry and diffractometry on Danish flint types were carried out by A. Tovborg Jensen, C. J. Wøhlk, K. Drenck, and E. Krogh Andersen [67].

The designation "flint" is used in Denmark for all types of sedimentary silica concretions that originate from cretaceous limestone and chalk formations. This flint is believed to have been formed when water percolation caused a concentration of the silica from sponge spicules, etc., deposited together with the limestone.

According to the petrographic descriptions the Danish flint consists mainly of calcite, opal, and chalcedony. The morphology and the relative frequency of the minerals suggest the following phases of development according to H. Gry and B. Søndergaard [66]:


limestone
calcareous opal chert (flint)
opal chert (flint)
calcareous chalcedony chert (flint)
chalcedony chert (flint)

all of which frequently do occur in Danish concrete aggregates.

The X-ray diffractometry investigation proved that chalcedony consists of α-quartz with a particle size of about 400 A, and that the opal consists of cryptocrystalline silica which, among others, contains 2-d-cristobalite. This investigation also offered results of quantitative measurements of the mineral composition, showing that the white, porous flint types may consist of some 90 percent of cryptocrystalline silica while the dense flint types generally consist of α-quartz entirely.

It appears from the above description of alkali-reactive minerals and rocks that the determination of their presence or absence in a certain aggregate or in a potential source of aggregates sometimes might be a very easy problem to solve for anyone familiar with the geological conditions of the area concerned, i.e., the origin of the aggregates in question.

Provided such surveys, however, prove or indicate the presence of alkali-reactive constituents, actual investigations of the materials will be needed.

As the foremost among methods, petrographic examination must be mentioned. In the first place, the disclosure of alkali-aggregate reactions gradually has attached to this method of examination the importance it deserves also in many other aspects of concrete technology. In the second place, it is the only practical means by which a detailed qualitative and quantitative knowledge of the nature of any aggregate may be obtained, thus representing a basis for the evaluation of results of other tests, examinations, and researches. Detailed descriptions of procedures for petrographic examination have been given in numerous papers, see, e.g., B. Mather [61], R. C. Mielenz and L. P. Witte [68], R. C. Mielenz [31], ASTM Designation: C 295–54, and in addition hereto various mineralogical handbooks, etc. E. Poulsen has [69] described the development of a technique for the preparation of samples for microscopic examination and of statistical methods for evaluation of the results of the observations made.

Originally, petrographic methods were used as a means of finding those types of rocks that might be the source of reactivity in an aggregate causing distress in concrete. As previously mentioned, petrography has now been applied for both quantitative and qualitative determination of the contents of rocks and minerals known as alkali reactive, in unknown or suspected aggregate. A few other methods, merely concerning a qualitative estimation of alkali reactivity of either aggregate samples or selected rocks or minerals, have survived the first year's intensive research applying different, already known principles and methods also for the studies of alkali reactivity. These are the gel pat test and the quick chemical test.

Gel pat test

This test was first described by Th. E. Stanton, O. J. Porter, L. C. Meder, and A. Nicol [33] and has later been elaborated by F. E. Jones and R. D. Tarleton [70]. Suitable pieces of an aggregate under investigation are embedded in a circular pat of neat cement paste with a ground face of each particle exposed at the surface of the pat. After curing, the pat is immersed in an alkaline solution and the exposed faces of the particles examined at intervals for exudations of gel. On some reactive rocks gel may develop very rapidly, on others more slowly. By the procedure recommended and described in detail in [70], importance is attached to the first 7 days of observation. However, a period of 28 days' observation is mentioned as useful in order to obtain a safe distinction between inactive and reactive materials. In the same paper some tests with British aggregates are referred to, by which the pats were removed from the alkaline solution after a 28-day period and then further observed during moist curing. The only British aggregate that showed gel exudation after 28 days in an alkaline solution was said to be a sandstone.

Quick chemical test

Familiar to everyone in the concrete research field is the problem of the practical builder who sometimes has to prove a certain quality of materials in the moment he is to commence concreting, and rarely at such an early stage that for instance, the 1-yr mortar-bar test or even a 28-day gel pat test is applicable. These circumstances have early inspired researchers to develop rapid methods for testing suspected aggregates. In table 7 is mentioned the later abandoned fluorescence and etching tests besides petrographic examination. The latter of course is reliable, provided that a skilled and well-trained petrographer with adequate equipment is at hand. In that case even a detailed petrographic analysis may be a question of only a few hours' work, and the costs will be accordingly small. However, as records of petrographic analysis do not directly express the reactivity of the examined materials and as untested rocks still remain to be tested, the exigency of a really rapid test of the alkali reactivity of aggregates still exists. As such a test the rapid or quick chemical test has been elaborated.

In [71] R. C. Mielenz, K. T. Greene, and E. J. Benton report their development of a method for a rapid chemical test. Today, more than 12 yr later, this article includes the essentials of what has appeared concerning the quick chemical method.

The aggregate was treated with an alkaline solution in order to determine:

1. The effect of the solution upon the aggregate and
2. The effect of the aggregate upon the solution.

Various alkaline solutions have been used, and amongst them those containing sodium hydroxide only are generally most destructive.

Re 1: The destruction was measured as weight loss and as degree of etch on polished surfaces. Unfortunately, only little correlation between the two processes and the mortar-bar tests was found.

Re 2: The changes in the solution have been determined as concentration of substances in solution, particularly silica, and changes in alkalinity. Measurements of silica dissolved prove that dissolution of silica is not quite correlated to deleteriousness. The reduction in alkalinity of the solution, which is effected by different aggregates, is widely variable. It would appear that this reduction to some extent is a measure of the efficiency with which the potency of the solution is utilized during the reaction. Since the alkali content of portland cement rarely exceeds 1.50 percent, the efficiency with which these alkalies liberate silica from the aggregate probably is a significant control of deleteriousness. Seventy-one different aggregates were ground to the fixed fineness of 0.15–0.30 mm, and a powdered material was also used.

In short, the procedure may be described as follows: 25 g of the crushed material was weighed and poured into a container of stainless steel. Upon addition of a solution of 25 ml 1*N* NaOH the container was closed airtight and placed in a thermostat for 24 hr at a constant temperature of 80 °C (the tests were tripled). Afterwards the content was filtered and in the filtrate Sc=dissolved SiO_2 as mM/l and Rc=reduction in alkalinity as mM/l were measured.

Since the ratio of released silica to alkalinity reduction appears to be significant, the factor Sc is plotted against Rc in a system of coordinates. On this basis the innocuous materials can be separated from the deleterious materials by a line whose locus approximates $Sc/Rc=1$, see figure 7.

The authors' working hypothesis is that the deleterious materials are characterized by their more effective utilization of the alkalies in the liberation of silica than the innocuous materials. For that reason Sc:Rc is less than 1 for innocuous materials and usually greater than 1 for deleterious materials. In order to certify the theory, comparisons with mortar-bar tests are made.

The mortar bars are produced by high-alkali cement (1.38 percent of equivalent alkali) and reactive aggregate combined in various proportions with crushed quartz.

The authors believe that the phenomenon of the pessimum proportion might represent the operation of two opposing characteristics of cement-aggregate reactions, namely: The tendency to increased expansion of the mortar as progressively more reactive particles are made available for attack, and the tendency to decrease in the silica-producing reaction as the available alkalies are more and more used up. From the continuation is quoted:

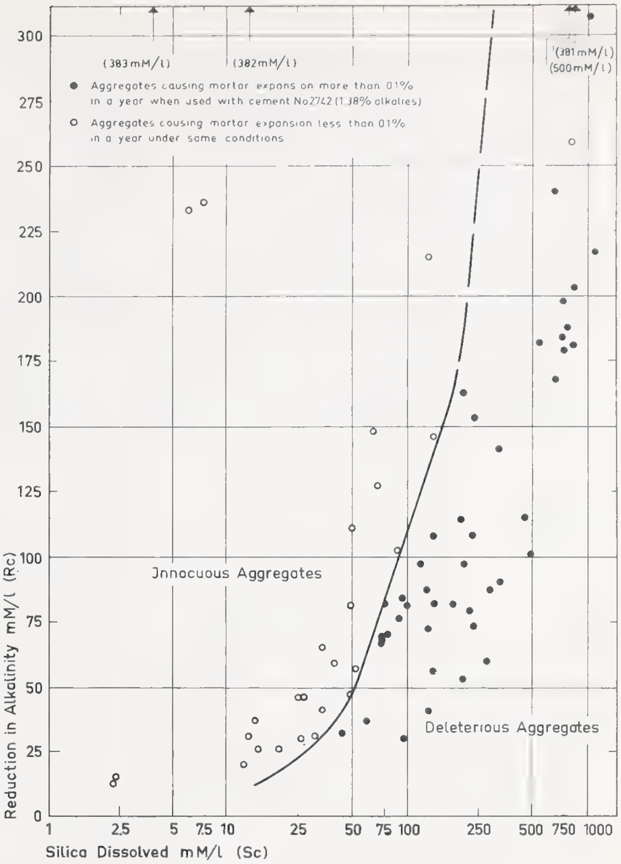


FIGURE 7. *Results of chemical test applied to American aggregates* [71].

"If these deductions are correct, then the pessimum proportion should be low for those aggregate materials which considerably reduce the alkalinity of the solution during the chemical test, and it should be large if the reduction in alkalinity is small".

By examining the 22 out of 71 aggregates the theories were found to be in accordance, see figure 8.

In [68] R. C. Mielenz and L. P. Witte summarize the five known test methods of identifying reactive concrete aggregates:

1. Petrographic analysis.
2. Quick chemical test.
3. Mortar-bar test.
4. Concrete-bar test.
5. Examination of concrete structures.

In the discussions the authors pointed out (see figure 9) that the areas for deleterious materials can be separated into two parts, of which the upper part includes materials which may be innocuous when constituting the entirety of an aggregate. The bordering line should be in accordance with a pessimum proportion of 20 percent.

Deleterious materials whose pessimum proportion is more than 20 percent (the lower part of the area) typically cause significant mortar-bar

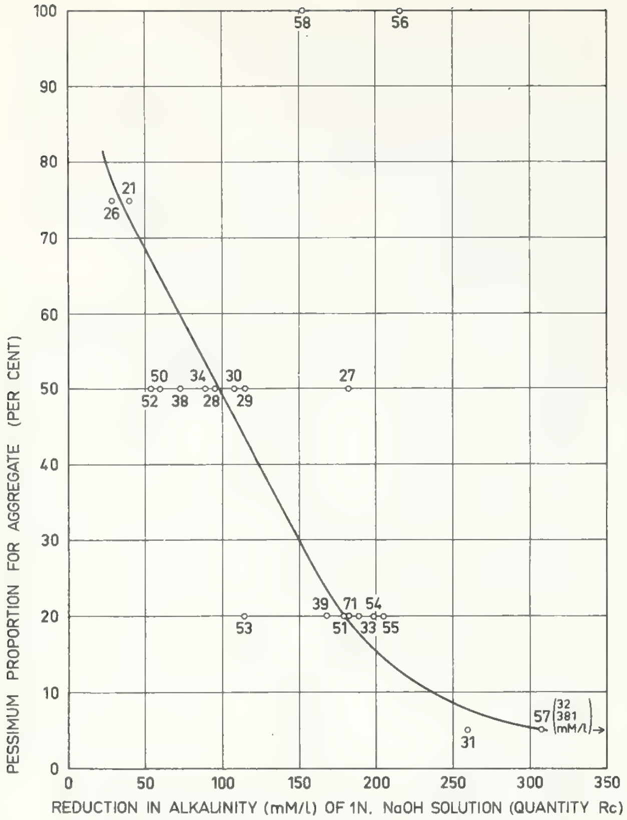


FIGURE 8. *Reduction in alkalinity in the chemical test as related to the pessimum proportion* [71].

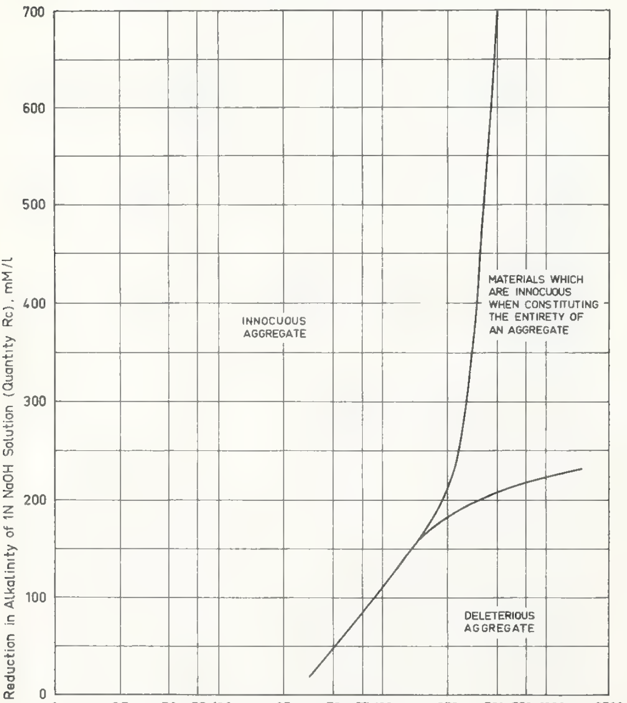


FIGURE 9. *Modified boundary lines* [68].

expansion when they constitute the entirety of the aggregate.

The quick chemical method has been worked out as a tentative standard method [72], ASTM Designation: C 289–57T, issued 1952, revised 1954 and 1957. The method is based on the work of R. C. Mielenz, K. T. Greene, and E. J. Benton [71], and the procedure is mainly the same as used by the authors.

The use of the *Rc* and *Sc* values for interpretation of the potential reactivity of aggregates is not, however, given in the standard, but in the specification for concrete aggregates, ASTM Designation: C 33–57 as:

1. If *Rc* exceeds 70 mM/liter the aggregate is considered potentially reactive if *Sc* is greater than *Rc*.
2. If *Rc* is less than 70 mM/liter the aggregate is considered potentially reactive if Sc is greater than $35+\frac{Rc}{2}$.

The boundary line between innocuous and deleterious aggregates is drawn in accordance herewith.

F. E. Jones and R. D. Tarleton [70] conclude that the rapid chemical test is a useful acceptance test. Thus, following the ASTM method of test, aggregates with *Sc*/*Rc* ratios of less than 1.5 can be accepted as safe. Aggregates with higher ratios will not necessarily be troublesome, and further examination by means of the expansion-bar test is required.

K. E. Haulund Christensen [73] thoroughly reviews the chemical test and, contrary to several other investigators who found the chemical test, mortar-bar test, and practice to be congruous, found inconsistency in 22 percent of the cases where Danish aggregates had been investigated. The author suggests a "Modified Chemical Test" which might improve the consistency. Thus the dividing curve is substituted by the line *Sc*=70 mM/liter, which makes the reactivity independent of the reduction in alkalinity. Consequently, the testing procedure becomes more simple, and the possibility of systematic errors is diminished. In figure 10, R. C. Mielenz's, K. T. Greene's, and E. J. Benton's data [71] are applied by plotting dissolved silica against expansion of mortar-bars.

R. C. Mielenz and E. J. Benton [74] carried out an analysis of the chemical test, ASTM Designation: C 289–54T, and arrive at the following conclusions:

1. The test is a useful means by which to evaluate potential deleterious reactivity of aggregates with cement alkalies. Its rapidity (2 days) is especially of credit.
2. The reproducibility of the method is acceptable.
3. When certain aggregate components, as, e.g., magnesium and iron carbonates (dolomite, magnesite, and siderite) or serpentine are present, the result may be a minor increase of the reduction in alkalinity and an increase of the concentration of

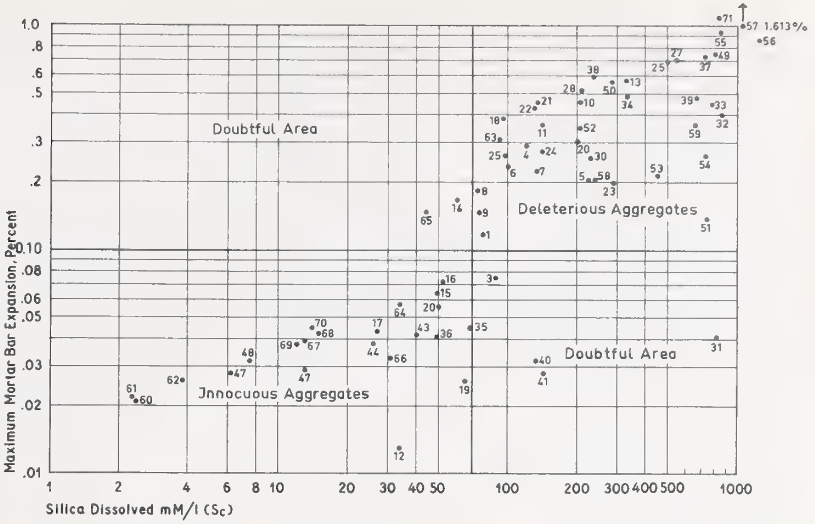


Figure 10. *"Modified chemical test."*
Dissolved silica (Sc) in relation to maximum mortar-bar expansion [73].

silica. A similar effect may be caused by calcite and may instigate an erroneous indication if the potential reactivity is marginal.

4. Because of this influence of certain minerals the evaluation of the chemical test should be supplemented by a petrographic analysis.

5. No changes in the standard procedure are suggested. It is recommended to investigate the influence of whether Rc is determined from the changes in the concentration of sodium and potassium or rather from the reduction of the titratable hydroxyl ion concentration.

B. Chaiken and W. J. Halstead [75] write upon the assumption that mortar-bar tests generally reflect the reaction in the actual structure. The mortar-bar tests were started before the ASTM standard method was developed. In these tests, bars with reactive aggregate in pessimum proportions seem not to have been included. Medium alkali cement (equivelent Na_2O percent 0.73–0.90) was used, and expansions <0.08 percent were considered indicative of nonreactive materials, expansions $\geqq 0.1$ percent as indicative of reactive aggregates, while expansions of 0.08 or 0.09 percent were regarded as questionable.

In the graphical presentation of the results of the chemical test an adjustment of the main boundary line is proposed. The deviation from the ASTM line might be explained by the fact that Mielenz and others obtained their results with a cement of a higher equivalent alkali content and used other limits for indication of reactive and doubtful aggregates.

The modified diagram is shown in figure 11. The diagram is divided into four parts. The area including the innocuous materials is separated by the line $Rc=60$ mM/liter, and the area including the deleterious materials is separated by a line similar to the boundary line shown in figure 9. On the bais of the available data, area B should be clearly indicative of safe aggregates. Chemical results appearing in this area should be reliable and no further tests are required. Materials falling in area A are generally safe but a petrographic analysis to disclose the possible presence of interfering minerals might be useful.

Area D contains reactive aggregates which are capable of producing excessive expansions in mortar bars. No further test would be necessary.

Aggregates in area C are classified as "highly reactive". The pessimum proportion is most

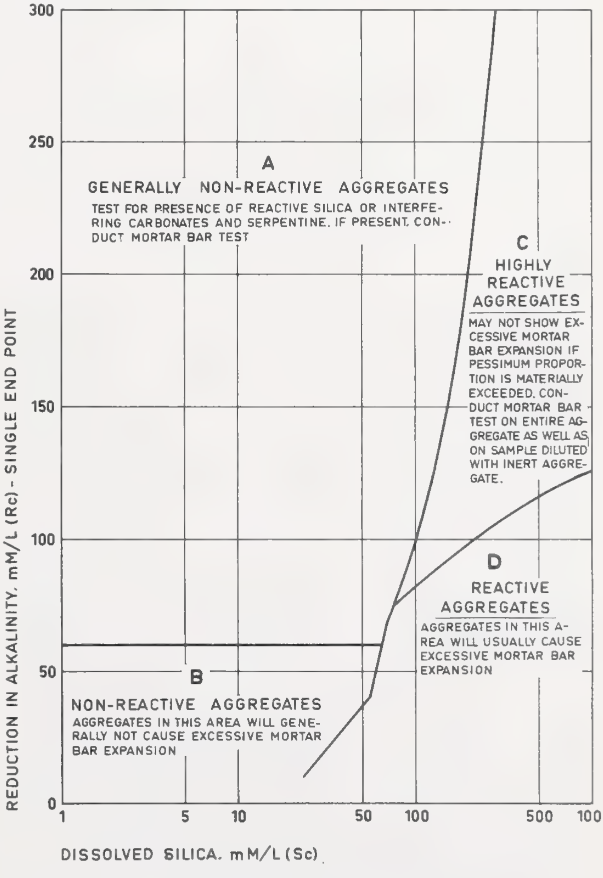


Figure 11. *Evaluation of results of chemical test for potential reactivity of aggregates* [75].

commonly about 20 percent for those situated in the lower parts of the area and less for those situated in the higher parts. Some are innocuous when constituting the entirety of the aggregate. If such aggregates are to be applied, mortar-bar tests with the aggregate in dilutions of 5, 10, 20, and greater percentages of inert materials as well as in its entirety, must be carried out solicitously.

In the summary of the above-mentioned paper the authors remark as follows:

"Nevertheless, the present criteria shown (in fig. 11) should broaden the usefulness of the quick chemical test and, in many cases eliminate the need for supplementing the chemical test with a long-term mortar-bar test program or tedious petrographic analysis."

The above review of literature on the quick chemical test leads to the conclusion that it is a helpful guide to determining the potential reactivity of aggregates. The test is of a qualitative character and does not indicate the size of the expansions that are to be expected in mortar bars or in structural concrete. The chemical test reveals chemical properties of an aggregate, viz., its ability for dissolving silica and reducing alkalinity.

It may be possible to apply the chemical test to a greater extent if the tracing of a relationship between the location of an aggregate in the *Sc—Rc* diagram and its pessimum proportion could be furthered.

Mortar-Bar Test

The methods of examination of concrete materials treated above are seen to enable a judgment of the potential risk that an aggregate will be alkali reactive. They even enable a judgment of whether an aggregate may be susceptible to intensive and rapid reaction or only to superficial and slow reaction. In other words, it is possible by means of the examination to characterize an aggregate as either "highly" or "slightly" reactive. This judgment may be based upon evaluation of petrographic data giving type, amount, and physical properties of reactive constituents in the aggregate, and also on solubility in alkaline solutions, clarified by means of the mentioned chemical tests. However, these approaches neither reflect the mechanism of alkali-aggregate reaction in mortar or concrete, nor imitate the mechanical effects which are the real evidence of the reaction and the cause of distress in structural concrete. Therefore, the necessity is obvious of testing combinations of cement, water, and susceptible aggregates as mortar and concrete.

This viewpoint is supported by regarding the generally applied terminology as characterization of alkali-reactive aggregates or of the reactions themselves. Reactive aggregates are generally differentiated as either "innocuous," "non-expansively reactive," etc., or "deleteriously reactive," "expansively reactive," etc. Similarly the reactions may be classified as either "harmless," "safe," "non-expansive," etc., or "harmful," "deleterious," "expansive." Most of these terms clearly refer to mechanical effects, either purely qualitative, as "deleterious," or quantitative, as "expansively reactive," and seem derived from observations and measurements of phenomena in the testing of mortar bars.

Development of the Method and Survey of Procedures

Before going into further discussion of the mortar-bar test method it seems appropriate to recall that the original investigation made by Stanton concerned the alkali reactivity of the sand fraction of the aggregates only (see [33]). Although reactivity of coarse aggregates was reported not much later than the findings by Stanton; see, e.g., R. F. Blanks in the discussion to [32] where chemical alteration of 6-in andesitic cobbles is mentioned, the already applied mortar-bar test proved advantageous in so many respects that coarse aggregates since then mostly have been tested and studied after crushing down to sand sizes. This practice has no doubt facilitated the examination and the tests, but this advantage seems in some cases to have been reduced by the disadvantage of a confused interpretation of the test results.

The very first experiments with mortar bars, referred to by Stanton [33], apparently only concerned observations of cracking and gel exudations. Expansion measurements have later on proved to be the probably most reliable means of standard testing of aggregate reactivity and a most valuable aid to studies of the reactions in research.

Furthermore, studies by means of mortar-bar tests have utilized measurements of tensile strength, bending strength and compressive strength; of dynamic modulus of elasticity; etc. Different procedures have been developed at different laboratories with respect to dimensions of bars, mix proportions and preparation methods, storage conditions concerning maintenance of suitable humidity and temperature, and various other technical details.

The more important discrepancies appear from the survey of procedures as given in table 10.

Design of Mortar-Bar Tests for Expansive Reactions

By now the percentage expansion of mortar-bar specimens after a suitable period of storage seems to be a generally accepted routine criterion on which the judgement of cement-aggregate combinations for concrete work is based. This scope of the mortar-bar test is aptly expressed in the first paragraph of ASTM Designation: C 227-52T:

"Scope

"1. This method of test is intended to determine the potential expansive alkali reactivity of cement-aggregate combinations by measuring the expansion developed by the combinations in mortar-bars under prescribed conditions of test".

A survey of elaborated procedures is given in table 10, and it appears that most procedures directly or indirectly fix such expansion-controlling factors

TABLE 10. *Survey of procedures of mortar-bar tests as applied by different authors*

	ASTM (USA) Standard	BRS (Great Britain) Research	CSIRO (Australia) Research	DNIBR/FLS (Denmark) Research
Dimensions (effective length).	1·1·10 in. (10 in.).	1·1·10 in. (10 in.).	1·1·11¼ (10 in.).	25·25·125 mm (105 mm).
Number of specimens per combination.	4 (2 from each of 2 batches).	at least 2 (a)	2	2
Grading of aggregate.	Fine: requirements of project specifications. Coarse: crushed and recombined in 5 fractions, sieve No. 4–No. 100 (20 percent each).	Crushed if necessary; recombined in 5 fractions, ³⁄₁₆-in–100 (B.S. sieves) (19 percent each, washed and dried)+5 percent passing 100.	Natural gravel used without further treatment (or crushed if undesirable large particles contained). For crushed stones 18–52 B.S.S. mesh fraction used alone.	Fine: Sieved and recombined in 5 fractions 4–⅛ mm mesh (20 percent each). Coarse: Crushed and recombined in 5 fractions as above.
Mix proportions.	Cement: Aggregate = 1:2.25; flow = 105–120.	Cement: Aggregate = 1:2 (a) w/c to obtain moist surface; min. alkali content in mix: 1.2 percent.	Cement: Aggregate = 1:2 w/o = 0.4–0.5 to obtain constant consistency.	Cement: Aggregate = 1:2; flow = 100 (w/c ∼ 5).
Molding.	Double or (preferably) single molds, thinly covered with mineral oil and outside sealed with a paraffin mixture.	Single molds without grease or oil (b).	Double or single molds thinly covered with mineral oil.	18 bars in one mold greased with oil and outside sealed with paraffin wax (c).
Placing and compaction.	Placed in two layers and compacted with tamper of medium hard rubber or impregnated oak.	Placed in thin layers and hand tamped with a square-nosed rod.	Placed in three layers each being carefully pressed down.	Placed in two layers and compacted by means of a tamper.
Storage.	Bars vertical over water and at 37.8 °C±1.7. Readings at 23 °C±1.7. Inverted position after readings.	Bars vertical over water and at 20 °C±0.5. Inverted position after readings.	Bars vertical over water and at room temperature (yearly mean 58.5 °F = 15 °C.	Bars vertical at 100 percent R.H. and at 38 °C. Inverted position after readings.
Records.	Expansion: Excessive when average exp.>0.05 at 3 months and average exp.>0.10 at 6 months. (d)	Expansion: Aggregate expansively reactive when exp.>0.05 percent in 6 months or exp.>0.1 percent in 12 months. Weight changes checked at readings. (e) Visual inspection of wet surfaces, gel deposits, cracks, etc.	Expansion: Dangerous when exp.>0.1 percent in 24 months. Visual inspection of damp spots, gel deposits, cracking, etc. (f)	Expansion: Potentially harmful when max. exp.>0.1 percent at 24 months. Visual inspection of damp spots, gel deposits, cracks, etc. (g)
References.	[72], p. 514–21, [44], [71], [82] and others.	[25], [70].	[21].	[73], [80], [81], [83].
Notes.	(d) The ASTM designation says nothing on criteria. The above information is found in [70].	(a) The specifications are partly from the "Recommended procedure for expansion bar test" [70], p. 44. (b) The amount of mortar mixed just filled molds. (e) In special series recordings bending strength were made, the expansion only recorded until the bending tests were effected.	(f) In special series the effect of expansion on tensile strength has been investigated.	(c) Since 1957 this method is considered obsolete, and only single molds are used. (g) After 24 months the flexural strength and compressive strength are determined.

as mix proportions and—to some extent—grading. Originally these factors appear to have been fixed at levels which were considered to be conducive to maximum expansion of mortar bars made of susceptible aggregates, when used in combination with cements of known alkali content. The expression "potential expansive alkali reactivity" in the passage quoted above may be a reflection of this view.

However, on the background of experiments made with systematically varied mix proportions and experiments measuring the influence of particle-size distribution, it may be questioned whether the rules adhered to by the mentioned procedures always allow us to observe the potential expansive alkali reactivity of the aggregates represented in the mortar bars.

The cement-aggregate ratio, for instance, is fixed at 0.5 or 0.44, whereas in concrete work this ratio may be lower. The influence of the cement-aggregate ratio on the expansion of mortar bars is not too well known, but it is imaginable that a lowering of this ratio in some cases may coincide with a movement towards pessimum proportion and thus induce a rise in expansion.

Most procedures fix the water-cement ratio indirectly in the neighborhood of 0.5 through requirements of flow. As mentioned later the water content of the cement paste is a factor influencing the mechanism of reaction, and as w/c in actual concrete work may be far from 0.5 one should be cautious in making general inferences based on a fixed water-cement ratio. Experimental work by H. E. Vivian [21] indicates that expansion of mortar bars (made with a uniform cement-aggregate ratio of 0.5) decreases rapidly when the water-cement ratio is lowered below the standard level of 0.4 to 0.5. It is, however, not known whether this result may be generalized as a law of nature.

From a practical point of view the most irrelevant requirement in the procedures is the rule that coarse aggregates should be crushed, sieved, and recombined to a linear grading curve. To this rule the ASTM standard has added:

"NOTE.—Coarse aggregate crushed to sand size may give accentuated expansion, owing to the increased surface exposed upon crushing the aggregate. Therefore, if coarse aggregate tested by this method produces an excessive amount of expansion, the material shall not be classed as objectionably reactive with alkali unless tests of concrete specimens confirm the findings of the tests of the mortar".

The note does not consider the opposite (and more perverse) possibility that coarse aggregates crushed down may cause small (safe) reaction, whereas concrete specimens with aggregates in the original particle size may produce dangerous expansion.

The standards for mortar-bar tests do not lay down rules as to which combinations of aggregates and types of cement are to be tested; the decision in this matter must be taken by the experimenter with a view to the purpose of the test series.

The purpose may be more or less specific. In section 4 of the ASTM standard cited previously it is stated that fine aggregates shall be tested in a grading meeting the specifications of the project.

In the design of such tests with the specific purpose of testing fine aggregates for a definite project, it should be remembered that deposits of gravel may exhibit great variations both as regards grading and the percentage of reactive aggregates within each fraction. Some information about this variability may be obtained by taking several independent samples from the deposit, sieving them, and making petrographic analyses fraction by fraction for each sample. As an example it should be mentioned that the percentage by weight of reactive materials (flint) in the fine aggregates from a Danish deposit varies between 12 percent and 30 percent (see B. Søndergaard [76]).

Under such conditions it may be very misleading to make all tests from one sample of fine aggregate, even if it is made representative of average conditions at the deposit by pooling a great many samples.

The variations in the deposit should be represented by a corresponding variation from bar to bar in the composition and grading of the aggregate. This recommendation springs from the fact that a slight change in the percentage of reactive materials may cause a move from safe to dangerous expansion, as illustrated in figure 12.

When the fine aggregate in a deposit is known to contain expansive reactive materials it may be questioned whether the mortar-bar tests for fine aggregates should be limited to the grading specified by the project.

From a survey of Danish deposits of gravel made by B. Søndergaard [76], it has turned out that on an average there is a very marked increase in percentage reactive aggregate with rising particle size of aggregates. By the mortar-bar test it may possibly be demonstrated in some cases that by excluding one or some fractions from the fine aggregates, the alkali reaction will take place without causing dangerous expansion.

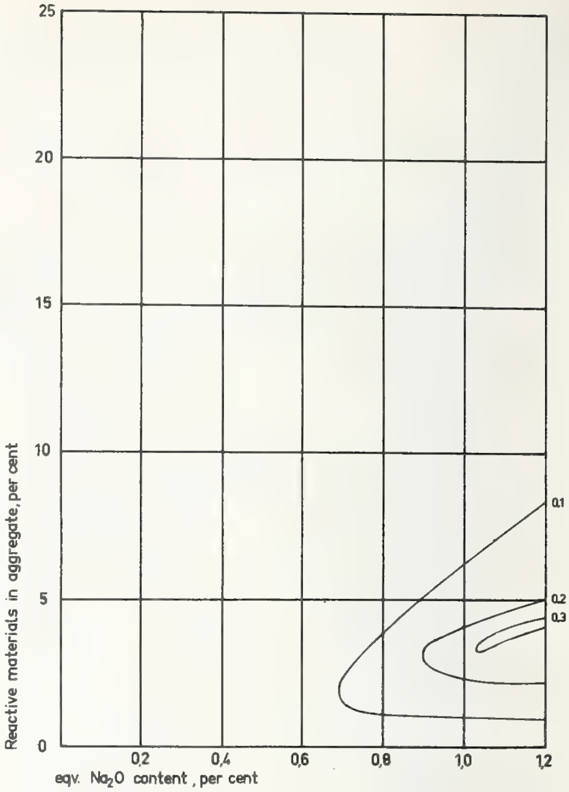


FIGURE 12a. *Expansion surfaces for five grain sizes of the same reactive aggregate (porous flint).*

The surfaces are indicated by iso-expansion curves, plotted as function of equivalent Na_2O, percent, and reactive materials in aggregate, percent.

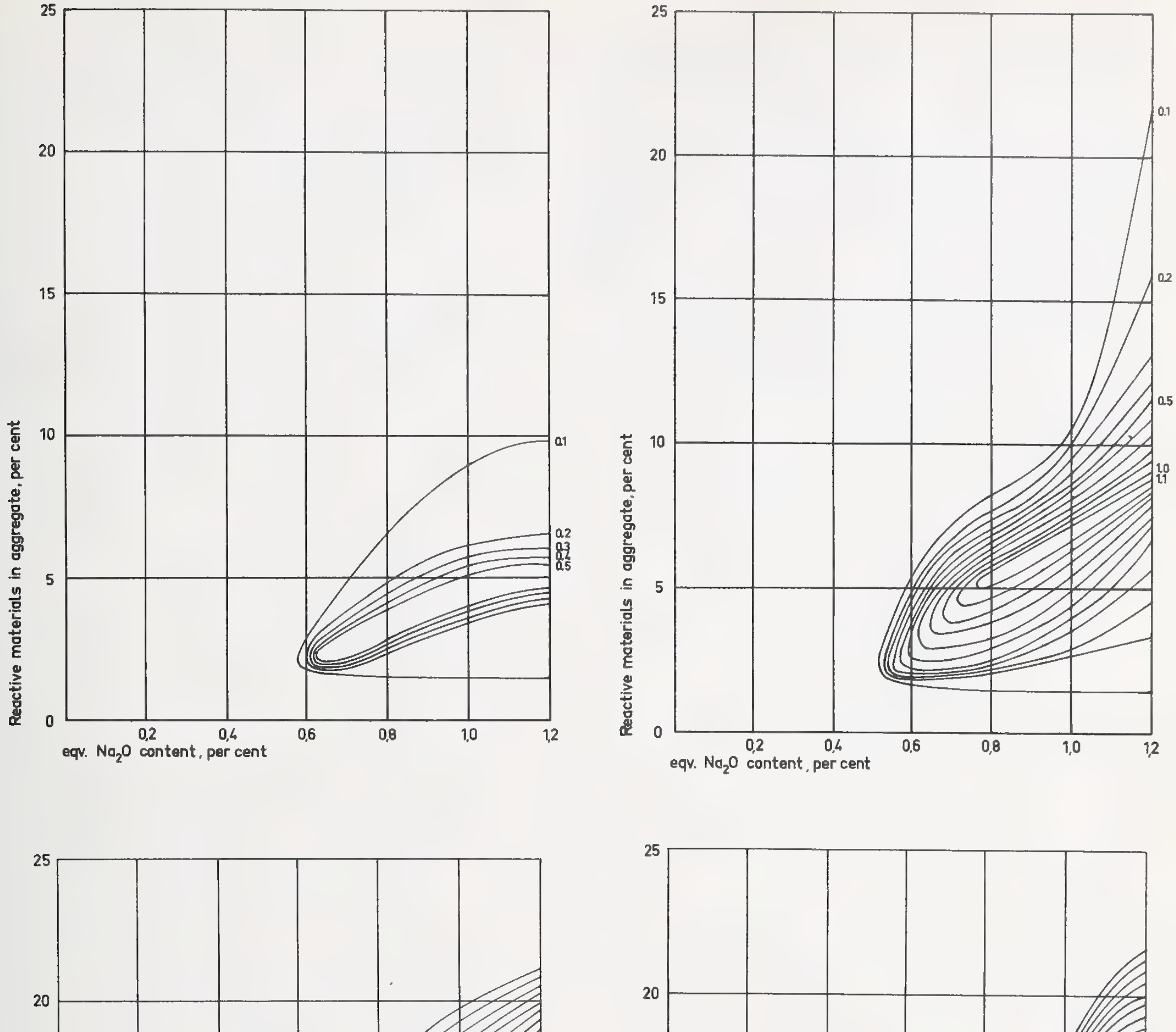
By changing the grading specifications in accordance with such results it may be possible to use fine aggregate from a deposit in the vicinity of an actual project, a solution which may be preferable from cost considerations. In this connection it should be remembered that specifications of grading may be varied within a very great range without damage to the concrete quality, if only the energy of compaction is changed correspondingly.

Evaluation of the Mortar-Bar Test

Contemplating the immense amount of data now available for studies of the still unsolved principal problems of alkali-aggregate reactions it may be profitable briefly to consider the possible findings which may result from the mortar-bar test. In table 11 the theoretical possibilities of the occurrences are presented and numbered.

TABLE 11. *Combinations of possible results of the mortar-bar test*

Aggregates classified according to petrographic or chemical analyses	Aggregates classified according to results of mortar-bar tests	
	Innocuous	Deleterious
Inactive	1	2
Reactive	3	4



FIGURES 12b,c,d,e. *Expansion surfaces for five grain sizes of the same reactive aggregate (porous flint).* The surfaces are indicated by iso-expansion curves, plotted as function of equivalent Na_2O, percent, and reactive materials in aggregate, percent.

The combinations No. 1 and No. 4 serve as background for the applicability of the test and do not need any particular direct comment. The combinations No. 2 and No. 3 represent complications in the sense of the test as a standardized method for testing susceptible aggregates. In table 12 are recorded possible explanations of their occurrences. Some of these explanations have been treated in the above discussion on the design of the mortar-bar test.

Although the first of the combinations in table 12 may be considered most exceptional, some attention should be paid to certain cement–aggregate reactions not definitely recognized as alkali-aggregate reactions. Expansive reactions in the cement paste alone most probably should not be considered possible, as long as the quality of the cement is subject to adequate supervision.

Table 12. *Complications to the mortar-bar test*

Combination	Explanation of occurrence
No. 2	1. Unidentified cement-aggregate reactions
	2. Expansive reactions in the cement paste only
	3. Unknown reason
No. 3	4. High porosity of cement paste
	5. High strength of cement paste
	6. Low alkali content of cement
	7. Few particles of reactive aggregate
	8. Non-expansively reactive rock types 8.1 Highly porous 8.2 Insignificantly attackable
	9. "Safe" reactions, i.e., production of sufficient amounts of non-swelling gels
	10. Insufficient duration of storage
	11. Unknown reasons

Combination No. 3, the occurrence of reactive aggregates that do not show expansion when tested according to standard procedures, is the most troublesome, because it may happen with any reactive aggregate and frequently does. Therefore, in practice it may lead to an acceptance of aggregates that should be avoided. Such test results may also cause confusion in research if not properly analyzed. The possible explanations listed as points 4–11 in table 12 comprise some of a physical character (4 and 5), some of a physico-chemical character (6–9), the time factor (10), and other possible but unknown reasons (11).

The influence of the mentioned physical factors, (4 and 5), has been investigated in particular by Vivian [77, 78], and by F. E. Jones [24, 25]. Vivian found that nonexpansive reactions in highly porous mortars may occur because of a sufficient space in the voids for the reacting particles and for the gel produced. However, a lack of sufficient free water seems also to be a possible influencing factor. The question of too few reactive particles (7) and the problem of whether reactions are "safe" or not is discussed elsewhere, and the possibility of meeting more or less readily reacting types of aggregates has been discussed earlier. Attention must be paid to the fact that very detailed analyses of results may be necessary in order to distinguish between "safe" reactions and "non-expansively reactive rock types". It is apparent that much work still remains to be done in this field.

The duration of storage is an important factor to consider when a known or a susceptible aggregate does not show any expansion in mortar bars. The practical application of the mortar-bar test inevitably suggests as limited a time as possible, i.e., as accelerated a test as feasible. Structural experience as well as many investigations by means of mortar and concrete bars suggest that expansion may develop with more or less delay under certain conditions, e.g., when low-alkali cements are used. Therefore, it is not possible as a rule to rely upon proportionality between time and expansion, and there may be a long time to wait for the first significant expansion to develop. Much work remains to be done before "no expansion" during a limited storage time may safely be interpreted as no expansion at all.

The influencing factor "unknown reason" (11) is mentioned, because in this field one may expect to meet so-far-undetected factors involved in the reactions and their mechanical effects.

Finally, the writers would emphasize that although the expansion proper has been given much attention as the quantitative result of the mortar-bar test, visual inspection of the appearance of the mortar bars should not be neglected. It appears from table 10 that recordings of damp spots, gel exudations, cracking, etc., are commonly prescribed as part of the useful observations which are obtainable from the mortar-bar test.

In T. E. Stanton's original paper [32] the formation of liquid drops accompanied by gel deposits was reported and suggested as indicative of reactivity.

A. R. Alderman, A. J. Gaskin, R. K. Jones, and H. E. Vivian [21] have reported detailed recordings of observed surface phenomena. The development of spots and random cracking has further been used as one of the means of studying the effect of alkali movement in hardened mortar. In this way the possibility of the migration of alkali through the mortar and the presence of the solution derived from excess mixing water as a continuous liquid medium throughout the mortar was clearly demonstrated.

Later J. K. McGowan and H. E. Vivian studied the correlation between crack development and expansion [79] and found a very good although not perfect correlation between expansion calculated from the mean number and width of cracks and expansion measured directly (correlation coefficient=0.92). It was shown that the expansion of mortar bars, which H. E. Vivian [21] observed to be preceded by the development of cracks and a loss of tensile strength, can be regarded as essentially due to the widening of cracks.

F. E. Jones and R. D. Tarleton [24] discussed the significance of various surface observations made on test bars, and arrived at the conclusion that such observations might be instructive as to reactivity of the aggregate.

As the writers also, in a more qualitative way, have outlined some applications of these principles [80, 81], it seems justified to consider the observations made by visual inspection an important part of the evaluation of the mortar-bar test. The more so, as these observations concern phenomena produced by or reflecting those internal processes, the result of which in the mortar-bar test is nominally measured as expansions.

Concrete-Bar Tests

As previously mentioned, Stanton first observed deterioration in the Bradley pavement in sections made with reactive sand. Later on, however, he also recognized a delayed expansion and cracking, where the reactive constituents were present in the coarse aggregates only (see [32], p. 110 of the discussion). Concurrent laboratory experiments showed that large specimens (6- by 12-in cylinders and 6 by 6 by 34-in beams) with reactive coarse aggregates expanded significantly between 1 yr and 18 months, independently of whether the exposure was dry, humid, or wet. On the other hand, 2 by 2 by 10-in bars (minus ¾-in aggregates) failed to expand when stored in water, whereas they expanded considerably in sealed containers (humid storage).

B. Tremper [84] reported experiments with mortar bars and concrete bars from the Washington area. Some mortar bars showed typical alkali-aggregate reactions when tested according to the standard mortar-bar procedure (sealed containers, constantly at 70 °F). Certain other aggregates did not expand except when concurrently with the standard storage they were exposed to cycles of freezing and thawing combined with wetting, reflecting conditions by local examples of structural failure. Similar results were found in concrete bars (4 by 4 by 20 in) cured in a dry room at 70 °F and thereafter exposed to freezing and thawing combined with leaching. Measurements of the dynamic modulus of elasticity were used for expressing the "durability factor". The conclusions of the experiments do not seem quite clear with respect to the characteristics of the alkali reactivity of the aggregates, whereas it is emphasized that high-alkali cement considerably lowered the resistance of mortar and concrete to freezing and thawing.

R. F. Blanks and H. Meissner [51] reported experiments with 3 by 3 by 15-in concrete bars, some of which had expanded 1.24 percent after 15 months in humid, sealed storage. It appeared that large open cracks, developed on the surfaces, extended only a short distance into the concrete, corresponding to what had been observed in structures. In the conclusions of this investigation it is recommended that coarse aggregates be tested by using the mortar-bar test after having been crushed down to sand sizes. In the discussion to [46] A. D. Conrow reported expansions obtained on concrete bars made with even exceptionally low alkali contents. The storage comprised:

1. Water curing at 70 °F,
2. Water curing at 160 °F and thereafter
3. Drying in an oven at 160 °F.

This rather extraordinary exposure was primarily intended to accelerate hydration in the cement paste to such an extent that expansive reactions were not veiled or eliminated by plastic deformations, but necessarily caused measurable expansion and disruption.

R. C. Mielenz and L. P. Witte [68] mentioned that attempts to develop a suitable procedure for moist-stored concrete-bar tests had been largely unsuccessful insofar as no dependable correlation with the mortar-bar test had been established. Meanwhile, natural weathering (wetting and drying, heating and cooling, i.e., purely physical factors) was found an important factor for development of disintegration in experimental concrete specimens. Subsequently a laboratory procedure was outlined, comprising exposure to cycles of wetting and drying of concrete bars. Bars 3 by 3 by 15 in were used. Wetting took place at 70 °F, drying at 130 °F, one cycle lasting one day. This procedure was very similar to the methods described by C. H. Scholer and W. E. Gibson [85]. Data from their experiments were found to indicate that expansion of more than 0.07 percent in 310 cycles or less should be regarded as reflecting structural failure in a similar exposure. It was also found—particularly with "sand and gravel aggregates" from Kimball, Nebraska—that excessive expansion and cracking occurred even with concrete made with low-alkali cement. It was herefrom concluded that "although alkali-aggregate reaction may contribute to the expansion developed during the test, the cement-aggregate incompatibility being evaluated is essentially independent of this reaction." This conclusion may be considered a confirmation of the results arrived at by Scholer by similar investigations of the Kansas sand-gravel aggregates, see [33], and by Scholer and Gibson in the above-mentioned paper on further investigations of the Kaw River aggregates. These aggregates were again investigated by W. Lerch [86]. From this paper it appears that they contained about 95 percent of quartz and feldspar, and about 5 percent of limestone and chert and occasionally opaline silica, volcanic glass, and other rock fragments. The quick chemical test proved the aggregate to be alkali reactive. Scholer's wetting and drying exposure was used on concrete bars, 3 by 3 by 11¼ in, cast with cements with the alkali contents ranging from 0.17 to 1.05 percent equivalent Na_2O. The deleterious reactions were found to produce alkali-silica gel, and by examination also reacted aggregate particles (opal) were observed. However, no relationship could be established between the alkali content of the cement and the expansion of the bars, and therefore it was also in this case concluded that some cement-aggregate reaction other than alkali-aggregate reaction might be a factor, and the alkali-aggregate reaction only contributory to the deterioration.

At this place the writers feel inclined to mention that in view of present-day theories on alkali-aggregate reactions, it is not obvious that these should be excluded as the primary cause of expansion and deterioration in the three papers treated above. Hence, the hypothetical "cement-aggregate reaction" in these cases may possibly be considered a result of inadequate means of investigation. This remark also pertains to similar investigations reported by C. H. Scholer and G. M. Smith [87], with the reservation that the reported inhibitive effect on the expansion of a certain amount of crushed limestone added to the coarse aggregate cannot immediately be explained merely by assuming the alkali-aggregate reaction to be the primary factor.

Th. B. Kennedy and K. Mather [88] presented a thorough study of correlation between accelerated laboratory freezing and thawing tests on concrete bars and weathering of concrete specimens of the same composition by natural, severe exposure on Treat Island, Maine. A discussion of this paper is not considered to be within the scope of the present report, because its main topic is purely physically determined disintegration. However, the paper should be mentioned as outstanding with respect to its treatment of the fundamental difficulties in transferring laboratory results to field concrete tests and vice versa. It is also of interest that the authors found evidences of beneficial effects of "mild" alkali-aggregate reaction, believed to have caused a measurable improvement of bond between slightly reacted chert pebbles in the coarse aggregate and ambient cement paste. This observation seems so far unique in the literature.

E. Trudsø [89] described freezing and thawing tests with 4 by 4 by 24-in concrete bars. Measurements were made by the resonant frequency method, and different Danish aggregates were tested in both lean and richer mixes. Supplementary visual inspections were made of evidences of deterioration, referred to as pop-outs, off-scaling, and map-cracking. It appeared that pop-outs developed over coarse aggregate particles of porous rock types (limestone and white, light cherts). Off-scaling was traced to the cement paste or mortar, and was the predominant effect in the lean mixture. The causal relation was less apparent for cracks. The porous, light cherts might have caused pop-outs (by enlargement) as a result of alkali-aggregate reaction in the bars as well as freezing and thawing, or maybe as a concurrent effect of both agencies. This may be the case too as regards the map-cracking. This remains to be further investigated by petrographic examination, etc. In principle, however, the attention paid to the visual phenomena is important, forming part of the necessary bridge from standardized mortar bars under defined exposure to field concrete that is subject to a complexity of disintegrating agencies.

C. E. S. Davis [90] presents a comparative study of the expansion of mortar and concrete. Mortar bars were used in the sizes 1 by 1 by 11¼ in and 2 by 2 by 11¼ in. The latter size was used also for concrete. Alkali-aggregate reactions were obtained by including 2.5 or 5.0 percent of opaline rock in the sand fraction, and in some cases also in the coarse fraction (½–³⁄₁₆ in). Alkali contents of the cement comprised 0.18, 0.81, and 1.18 percent equivalent Na_2O, respectively. The paper contains a great many interesting observations and comments, among which are:

1. Bars with inactive aggregates did not expand, while all bars with opal cracked and expanded, the more so the higher the alkali content of the cement. Rates of expansion were greatest at first and slowed down after a few months' time. Rates depended on the season, being greatest in summer.

2. A certain absolute minimum alkali content of the cement (0.4 percent equivalent Na_2O) was necessary to obtain expansion in mortar bars. Increase of the amount of opal in aggregates necessitated a greater alkali content. Concrete bars needed more alkali for expansion than did mortar bars.

3. Larger mortar bars began to expand slightly later than smaller ones, but after 3 months' time their rate of expansion was the greatest. The large bars developed the widest cracks by expansion.

4. Concrete bars with inert coarse aggregate cracked and expanded later than mortars. The relationship with respect to the time factor was found expressed by the equation:

$$T=\frac{t^2}{11}$$

in which T=time of significant expansion of a concrete bar, t=time of significant expansion of a mortar bar made up of the mortar part of the concrete.

5. Expansion develops as a result of internal cracking, which again is caused by the swelling of reacted particles. Measurable expansions demand that cracks cross the line joining the inserts in the ends of a bar. Therefore, the size of a bar, particularly of the cross section, is a factor in the ultimate expansion, the delay before, and the rate of an expansion.

6. Coarse, inert aggregate particles form a delaying or preventive barrier against expansion in the mortar section. Oriented rods cause cracking to take place parallel to the longitudinal direction of the rods. Reinforcement should be expected to give this effect in structural concrete. Rods decrease expansion, as does coarse inert aggregate. Coarse, reactive aggregate particles ease or increase expansion, particularly with small amounts of alkalies. Concrete made with cement with as little as 0.4 percent equivalent Na_2O may expand within a few years, if the aggregates contain small amounts of coarse opaline particles.

7. The time factor in the empirical relationship for expansion of mortar and concrete, respectively, can be established so that mortar-bar tests any-

where may be reliable for the prediction of the behavior of comparable concrete with any reactive aggregate.

Inspection of Structures

Many examples of deterioration of field concrete due to alkali-aggregate reactions have probably been diagnosed merely by means of examination and testing of the used aggregates and cements in connection with more or less rough field inspections. Other cases have been reported where supplementary minute examinations of the deteriorated concrete have been carried out, particularly by applying petrographic methods for the studies of the macrostructure and the microstructure of the concrete. Outstanding examples of such investigations have been reported by, for instance, D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45], R. C. Mielenz and L. P. Witte [68], B. Mather [57], K. Mather [91], and L. S. Brown [58].

There is but little doubt that in many cases only such examinations can furnish the proof that deleterious alkali-aggregate reactions have either taken place in the concrete or have not contributed to observed deterioration, thus confirming or eliminating hypotheses that might have been established on the basis of tests and examinations as previously discussed.

The petrographic examination of concrete structures and concrete samples, etc., is also treated by G. M. Idorn [92]. An even more extensive report on recent investigations in Denmark by the same author is given in [93]. It is emphasized that these papers deal particularly with description and interpretation of phenomena of deterioration in existing concrete (or mortar) and do not, at least directly, represent means of correlation between the above-described tests of susceptible materials and the future behavior of structures made with the materials in question. This problem comprises studies of e.g., model laws, characterization of exposures, microclimates, etc., and represents another rather unapproached field, probably rather because the difficulties are great than on account of overlooking its importance.

Figure 13, quoted from G. M. Idorn [94], may be referred to as an example. There serves as the basis for the presentation of the figure the fact that the expansion of mortar bars, stored under idealized exposure conditions, is a generally used measure of deterioration, both by sulfate attack in sea water and by alkali-aggregate reactions.

However, the aggressive reactants in sulfate reactions originate from the ambient medium, and the deterioration will progress inward from the surface of the bar, while alkali-aggregate reactions are internal reactions of the original concrete constituents. Hence, the applied measures actually cover quite different phenomena of reactions. Severe sulfate attack on a great concrete member under natural exposure must be expected to result in expansion and disruption of a surface layer that ultimately may spall off. The mortar bars regarded as "models" would then be models of the surface layer only, whereas the total volume of the member would be decreasing. It is otherwise in the case of harmful alkali-aggregate reactions in a great concrete member. Enlargements of the whole mass take place, reflecting expansions in any section of the member, and the mortar bars may be considered a rather direct "model" of the true situation, at least qualitatively.

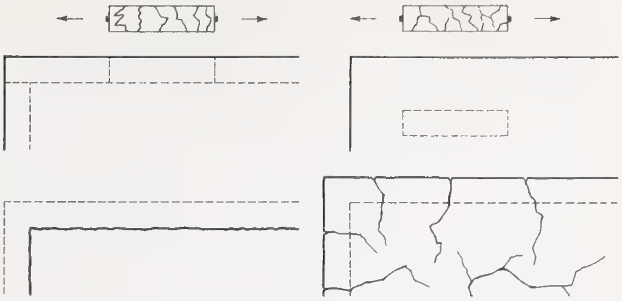


Figure 13. *Causes of weathering and mechanical effects in tests on mortar prisms and in concrete under natural conditions.*

Sulfate attack (left) and harmful alkali reactions (right). From [94].

These remarks are intended to point out that the possibilities for erroneous interpretation of the results of experimental work are considerable if due regard is not paid to both the mechanisms of the investigated reactions and the practical conditions that are believed to be imitated by the experiments.

Mechanism of Reactions

W. C. Hansen [95] ascribed the expansive reactions to pressure developed by osmosis, suggesting that the hardened cement paste around a reacting particle acts as a semipermeable membrane. H. E. Vivian [96] claimed this hypothesis to be improbable and explained the expansive pressure to develop as water is imbibed in the still rigid gel. D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45] reported experiments actually proving that cement paste may act as semipermeable membrane for a sodium silicate (waterglass). Pressures more than 550 p.s.i. were obtained within 4 days. W. H. Parsons and H. Insley [97] claimed that pressure causing cracking develops in pores that are filled by liquid gel from reacting aggregate particles and that the pore walls form the necessary semipermeable membrane. McConnell, Mielenz, Holland, and Greene [45] opposed the latter hypothesis and claimed that pressure is primarily exerted by the gel in the reacting aggregate particles and that cracking caused by expansion takes place early during the softening of the gel.

T. C. Powers and H. H. Steinour in 1955 [98] discussed the chemical reactions and the way in which they caused expansion.

The body-building structural arrangements in silica minerals are due to links between the silica molecules. These may be imagined as tetrahedra with a silicon ion (of 4 valences) in the centre, and four oxygen ions (of 2 valences) each in a corner of the tetrahedron. Each oxygen ion is common to two tetrahedra, the charge thus being satisfied. The crystalline silica minerals are characterized by strictly defined, oriented-pattern arrangements of the tetrahedra. The noncrystalline silica minerals are characterized by a random network of tetrahedra with numerous, irregular spaces between the molecules or groups of molecules.

In an aqueous medium the surface of a silica particle will be slightly acid. Each silica tetrahedron at the boundary holds one oxygen ion with an unsatisfied negative charge, and the corresponding silicon ion similarly holds one positive charge. Hydrolysis, therefore, takes, place, H^+ joining with the available oxygen ion and OH^- going to the positive silicon ion. In this way a surface layer of hydroxyl groups is produced. The H^+ ions are bound less firmly than are the OH^- groups, and therefore the surface of any silica particle in aqueous surroundings will be slightly acid. This acid character is negligible in crystalline silica in which the specific surface is very low. In microcrystalline to cryptocrystalline silica, and most extreme in the case of noncrystalline colloidal silica minerals, the hydration will be more and more pronounced due to the greater specific surface containing considerable amounts of unsatisfied ionic charges.

If the ambient medium is a strongly alkaline solution, not only will surface hydration take place, but also the internal silicon-oxygen-silicon bonds will be severed, and accordingly the substance may be peptized. Orderly crystallized silica, as quartz, is under normal conditions not attackable in this way.

Referring to experiments by Kalousek, Vivian, and van der Burgh, a hypothesis on how the above reactions may proceed in concrete was also outlined, i.e., when attackable silica particles are placed in a cement paste holding a caustic solution with both calcium and sodium (potassium considered equivalent sodium) as the available cations.

It was found that in the boundary layer of a reacting silica particle a lime-alkali-silica complex is produced, and that this layer can prevent further diffusion of calcium ions to the still unattacked interior parts of the particle where the reactions proceed by further imbibition of sodium and water, producing an alkali-silica gel without lime.

Hence, the surrounding layer of lime-alkali-silica complex acts as a semipermeable membrane, and the diffusion through this causes osmotic pressure to develop.

Reference was also made to the clay minerals of the montmorillonite type that expand by taking up water in the lattice. If water is prevented from entering by applying just sufficient pressure to the solid substance, the counteracting pressure may be considered osmotic pressure developed without the presence of a semipermeable membrane.

It was further stated that the alkali-silica gels imbibing water are of the so-called unlimited-swelling type, due to the peptizing effects of alkali hydroxides, while the lime-alkali-silica gels and also lime-silica gels (cement gel) are nonswelling or only limited swelling.

The presented explanation of the chemical reactions and of the mechanism of expansion due to the reactions seems to agree with the suggestion by W. C. Hansen and others that hydraulic pressure of osmotic origin develops, maintained by the walls of reacting particles acting as semipermeable membranes. However, it also seems to cover the opinion of Vivian and others that no semipermeable membrane need be involved, the expansion being due to swelling of the solids only.

It was furthermore mentioned that when alkali-silica gel exudes from reacting particles into nearby cracks or voids, osmotic pressure may develop in such deposits by further diffusion, the cement paste itself acting as a semipermeable membrane.

A concurrent paper by the same authors [99] further discussed the conditions determining whether the reactions lead to expansions or not, in which latter case they are designated nonexpansive or safe.

Reviewing older experimental data, the authors found that the quantity and the particle size (i.e., total boundary area) of the reactive constituents in aggregates are factors, and that each combination of these characteristics determines a safe concentration of alkalies in the cement paste.

The hypothesis was put forward that the lime-alkali-silica gel initially formed in the boundary of a reacting particle adsorbs lime and alkali from the ambient paste. The relative amounts of adsorbed lime and alkali are controlled by the alkali content of the solution in the cement paste. By diffusion, adsorbed lime and alkali move through the reacted layer to attack the silica in the interior of the particle. Lime can diffuse fast enough through the layer to secure continued production of the nonswelling gel if the ratio of adsorbed lime to adsorbed alkali in the external layer is kept high enough. The alkali concentration of the cement paste, therefore, must be low. If the ratio of adsorbed lime to adsorbed alkali in the outer layer of the nonswelling gel is not kept high, lime cannot reach the reaction site sufficiently fast, and a pure alkali-silica gel is produced, which swells by imbibition of water and causes cracking and concurrent expansion of the surrounding paste.

Even in a safe reaction some of the initially reacted alkali is released and thus made available for deeper reaction in the silica until the whole particle is altered to a lime-silica-alkali complex. In such a safe reaction some silica must diffuse out of the particle and react with lime and alkali outside, i.e., in the paste.

The authors found this hypothesis to some extent supported by investigated, available data, and concluded that with cements of up to about 0.6 percent of equivalent Na_2O the alkali concentration appears to be low enough to secure safe initial reactions. The continued reactions can be safe only when the quantity of reactive silica is at minimum or more than a certain amount, depending on the alkali concentration and the fineness of the reacting particles. With high-alkali cements safe reactions will occur only if the reactive silica presents sufficient surface area. If the silica particles are relatively uniform and not of extreme fineness. the required ratio of silica to alkali for securing safe reactions is much higher than for low-alkali cements.

The effectiveness of pozzolanic additions for prevention of harmful reactions is due to their large specific surface which provides an almost initial decrease of alkali concentration, so that the reactions must proceed in the safe phase.

In mortar bars, as well as in concrete, reactions can be expansive even with low-alkali cements when the aggregates do not meet the requirements above stated.

It was mentioned in the paper that these circumstances may be present in the wetting and drying test developed by Conrow (further treated later in this report). Similarly these considerations should be remembered as regards the sometimes stated "lacking correlation between alkali content of cements and expansions of mortar bars or concrete bars in standard tests".

Ervin Poulsen [50] further treated the established analytical relationships, using the experimental data presented by D. O. Woolf [48].

G. Verbeck and Ch. Gramlich [100] by means of an osmotic-cell technique investigated the theory of osmotic pressure by formation of alkali-silica gels of the viscous and the solution type. The influence of various factors on the magnitude of the pressure was studied. The results implied among others that "there should exist some intermediate water-cement ratio of the paste at which a maximum rate of expansion or ultimate expansion should be observed as a function of this variable alone and that the observed expansions would be less for either lower or higher water-cement ratios".—In other words, in alkali-aggregate reactions there may also exist "pessimum proportions" as regards the water content of the cement paste.

In general, the results of these studies seem to corroborate the hypothesis put forward by Powers and Steinour.

K. E. Haulund Christensen [73] concluded from a discussion that: "It is reasonable to suppose that the prerequisite of a safe reaction consists not only in a sufficiently great diffusion velocity for Ca^{2+} towards the reaction zone, but also in the degree to which the gel is capable of retaining a sufficiently high concentration of SiO_3^{2-} in the pores."

R. G. Pike and D. Hubbard [101] reported experiments by an interferometric technique, suggested to confirm the inhibitive effect of calcium hydroxide on alkali-aggregate reactions.

The rate of attack on opal of sodium hydroxide plus calcium hydroxide was found to be about ⅕ the rate of attack of sodium hydroxide alone. It was also found that the magnitude of the pH of the attacking solution is a determinative factor of the reactions, and it was suggested that the ionic charge of aggregates and cement, respectively, may be of influence. These observations, no doubt, ought to be given much attention in future research on the nature of the reactions.

R. G. Pike [102] reported some very interesting measurements with a special pressure cell, showing that alkali-aggregate reactions in cement pastes and mortars may develop pressures in excess of 2,000 psi. The paste or mortar was packed in a small steel tube around which was wrapped a strain gauge which served as the measuring device. The high pressures were obtained in about 140 days when a high-alkali cement was used and 4 g of opal (No. 16 to 20, U.S.-sieves) was embedded in the paste.

The late R. A. J. Bosschart and R. Wyatt [103] presented an interesting account of the nature of the chemical aspects of alkali-aggregate reactions, emphasizing the structures of partly microcrystalline quartz modifications and the role of OH^- ions in the destruction of reactive aggregate particles.

From the above review of research on the mechanism of alkali-aggregate reactions it appears that so far very few have dealt with the relative reactivity of different types of siliceous aggregates, or presented the relationships between the molecular structure of the silica minerals and their behavior under attack by alkalies. Neither has the influence of the particle size of coarse aggregates on the mechanisms and on the effects of reactions been particularly studied.

These two factors: (1) type and structure of reactive minerals and (2) behavior of coarse size aggregates, therefore, ought to be considered prominent objects of attention in further basic investigations of the nature of alkali-aggregate reactions. The not yet clarified influence of the water content of the cement paste and of variations in water contents should also be borne in mind. All these matters are of obvious importance as regards the behavior of field concrete under natural exposure.

Unidentified Cement-Aggregate Reactions

According to previous passages in this paper several authors in the United States of America have reported certain deleterious cement-aggregate reactions, considered to differ from the ordinary alkali-aggregate reactions. The nature of these peculiar processes has so far not been clearly described. The deleterious structural effects of both types of deterioration seem to be quite alike, consisting in expansions, map-cracking, and popouts. This similarity indicates that fundamentally the mechanism of the reactions should be the same, i.e., developing chemical alteration of aggregate particles, which lead to enlargements causing pressure and eventual structural disruption.

Summarizing the major papers on cement-aggregate reactions it seems justifiable to divide them roughly into two groups.

To the first group belong those reactions that are believed not to be traditional alkali-aggregate reactions, mainly because no correlation has been found between alkali content of the cement and expansion of mortar-bar or concrete-bar specimens and because the standard mortar-bar test has failed to reveal expansive reactivity of aggregates that have performed badly in field concrete.

The second group of cement-aggregate reactions comprises those that are believed not to be alkali-aggregate reactions because no alkali-reactive rocks at all, or only negligible amounts thereof, have been found by petrographic examination of the aggregates, and because alkali-silica gels and reaction rims on aggregate pebbles have not been met with by petrographic examination of affected concrete. Moreover, the standard tests for alkali reactivity have failed to give positive indications.

The most concentrated occurrences of unidentified cement-aggregate reactions of the first group seem so far to have been recognized in Kansas, Nebraska, and Wyoming, U.S.A., and to concern concrete with certain "sand-gravel" aggregates from beds of some of the major rivers. In other passages of this report references to the investigations of the troubles met with in these areas are made several times, when comparisons to alkali-aggregate reactions have made it natural to do so. Some concise comments, however, on the investigations by A. D. Conrow, reported in [40], seem here in place also because these studies have formed the basis of a standard procedure for evaluation of reactivity of aggregates by a concrete-bar test, ASTM Designation: 342–55T.

The sand-gravel aggregates concerned were deficient in coarse aggregates, and much of the concrete in pavements, bridges, etc., therefore, had been cast with a somewhat high cement content. The tests were interpreted as showing that expansion in the concrete was not related to the alkali content of the cement and that low-alkali cements did not assure against damage. The studies did not comprise petrographic examination of aggregates, but these are designated "siliceous". In some tests coarse limestone fractions were added. This addition was found to decrease the expansion of concrete bars. The observed expansion of the sand-limestone concrete was found to be due to the siliceous sand component.

It was considered a strong possibility—though not directly supported by observations—that the potential release of calcium hydroxide by hydration of the cement and the rate of this release might be an accelerating factor.

The test procedure, elaborated after a great number of experiments had been made, comprised after 28 days water curing at standard temperature:

1. Seven days storage in water at 130 °F.
2. Cooling and storage in water at standard temperature for 20–24 hr.
3. Seven days drying at 130 °F.
4. Indefinite storage in water at standard temperature.

Adequate measurements of length and of fundamental vibration frequency by the sonic method for Young's modulus of elasticity are to be made at intervals during the above storage.

W. Lerch in a recent paper [104] has reported further studies of the problem. In this work the sand-gravel aggregates are characterized as predominantly siliceous, being essentially composed of granite, feldspar, and quartz. "They contain smaller quantities of sandstone, rhyolites, andesites, siliceous limestone, and chert. The relative quantities of these various constituents vary somewhat along different rivers and from different locations along the same river. So far as deleterious reactivity with cement alkalies is concerned, these aggregates range from innocuous to slightly deleterious, depending upon their content of rhyolite, andesite, chalcedonic or opaline cherts, and siliceous limestone. An examination of concretes made with these aggregates usually reveals the presence of some alkali silicate gel or other evidence of alkali-aggregate reaction".

Concerning the nature of the reactions the following is stated in the same paper:

"The deterioration of the sand-gravel aggregate concretes involves a chemical or physical phenomenon that is not yet clearly defined. Although the alkali content of the cement appears to contribute to the deterioration of the sand-gravel aggregate concretes, this development cannot be ascribed completely to alkali-aggregate reaction of the type described by Stanton. Mortar-bar tests made with the sand-gravel aggregates in combination with cements of different alkali contents do not develop expansion related to the alkali content of the cements. Furthermore, the use of low-alkali cements does not inhibit the deterioration of the sand-gravel aggregate concretes as it does in concretes with truly alkali-reactive aggregates".

For many reasons the writers do not feel inclined to comment on the statements referred to. The *locus in quo* is far away, and more papers offering the wanted information and adequate explanations of the problems may be on the way and may throw light on the unsolved problems, even before the present report is published. It seems right, however, to point out a few facts already apparent from the published data.

A. D. Conrow mentioned that the sand-gravel concretes often had been cast with a somewhat high cement content. Sometimes, however, this may have eliminated the assumed effect of using low-alkali cements.

It was also stated that no relationship could be established between the alkali content of cement and expansion of mortar bars and concrete bars. However, it appears that by the tests and experiments, the types, amounts, and grain-size distribution of reacting particles in the aggregates have not been determined, let alone selected. Referring also to the above statement by W. Lerch concerning the origin and composition of the aggregates, it seems rather possible that unregistered and not recognized variations in the composition of the concrete, including amounts of available alkalies and characteristics of reactive constituents of aggregates, etc., so far have prevented the lacking correlations to be disclosed. Expansion with low-alkali cements (and even without high cement contents) are even now known to be a possibility where only minor amounts of certain reactive constituents are present. In some cases these "minor amounts" have been less than one percent by weight of the total aggregates, dependent on grain-sizes, types, etc.

It seems also striking that, according to W. Lerch, alkali-silica gel may be expected to develop during the reactions.

In the opinion of the writers these circumstances tend to raise an argument for more elaborate studies to be presented before any major difference between the described processes and the traditional alkali-aggregate reaction is so definitely stated that the particular designation is motivated. Differences appearing from the empirical testing methods only, should, a priori, be considered just as well to reflect incapability of the testing methods as different processes of reaction.

Two reports on cement-aggregate reactions in Canada have been prepared by E. G. Swenson. One of the cases, treated in [16] presumably may be considered as covered by the above remarks on the American cases; the other seems somewhat different as it appears from the treatment in [105]. The deterioration, which as regards the mechanical effects, was quite similar to the result of alkali-aggregate reactions, was found related to a coarse argillaceous dolomitic limestone aggregate. The absence of alkali-silica gel and reaction rims, and the fact that reactivity of the aggregates failed to be revealed by the ASTM standard tests, made it necessary to investigate other possible factors. The Conrow test, ASTM Method C 342–55 T, did not give sufficient further information, although expansions were obtained with some sands under investigation. Exposure tests with concrete beams, however, involving wetting and drying and freezing and thawing, indicated that abnormal expansion occurred preferably under the influence of moisture and temperature. It was also indicated that expansion due to the coarse limestone aggregates was sharply influenced by the alkali content of the cement. No doubt future papers on this matter will receive much attention.

For obvious reasons the writers prefer to finish the present passage without a general evaluation of the presented data, but rather to quote some remarks by B. Mather in the discussion to the above-treated paper by A. D. Conrow:

"Mr. Conrow implies that the phenomena observed are limited, at least as far as is at present known, to concrete made with certain natural siliceous aggregates from the Central Great Plains region of the United States. He concludes that there is a strong possibility that the abnormal expansion is related in some way to the amount and rate of development of calcium hydroxide during cement hydration, and that the alkalies (soda and potassa) act as catalysts. He finds that the abnormal expansion can be prevented or much decreased by the use of a proper amount of suitable pozzolan. He seems to suggest that possibly the principal function of the pozzolan is the obvious one of using up the calcium hydroxide. Since he states that it has been quite definitely demonstrated that the abnormal expansion is not consistently related to the alkali content of the cement, he appears to imply that the phenomena involved are significantly different from what now might be called the 'classical' alkali-aggregate reaction.

"Mr. Conrow suggests that if the calcium hydroxide is responsible for the expansion, the carbonation of the hydroxide might be expected to prevent or inhibit the expansion. In this connection reference may be made to the experiments by Gaskin, who investigated the possibility of preventing alkali-aggregate reaction by carbonating the sodium and potassium hydroxides by exposure to carbon dioxide. His results led him to conclude that the presence of an excess of carbon dioxide prevented the expansion, apparently by the formation of relatively impermeable protective shells of calcite around particles of reactive aggregate.

"It has been observed in this laboratory that all samples of concrete or mortar that have undergone alkali-aggregate reaction, and that have been subjected to microscope examination are characterized by materially reduced quantities of crystalline calcium hydroxide. The presumption that the alkali-aggregate reactions themselves are responsible for this apparent consumption of calcium hydroxide is therefore suggested. It has been indicated that the pozzolanic reaction which consumes calcium hydroxide prevents or inhibits the deleterious effects of the alkali-aggregate reaction. If it may be further assumed that the presence of crystalline calcium hydroxide is necessary to the progress of the alkali-aggregate reaction, then the interesting possibility, which Mr. Conrow has mentioned, is suggested: that the mere consumption of calcium hydroxide by reaction with a pozzolan is sufficient to explain the beneficial effects of pozzolans in preventing abnormal expansion.

"Mr. Conrow indicates that additional study is needed. The writer would like to propose several items, the study of which might be expected to shed light on these and related problems:

"1. Thorough petrographic examination of the aggregates that are involved, with particular reference to differences between them and apparently similar materials that do not behave similarly and to differences between the aggregates before and after they have been used in specimens that have undergone abnormal expansion.

"2. Microscopic examination of the concrete at various stages in the development of the expansion to determine if detectable changes occur progressively in the aggregate particles, the hydration products of the cement, or in the cement-aggregate texture.

"3. Subjection of other cement-aggregate combinations to the test exposure to determine if similar results may be obtained."

The extensive work of the Danish Committee on Alkali Reactions in Concrete under the joint auspices of the Academy of Technical Sciences and the Danish National Institute of Building Research is the background for the present general report.

The preparation of the report has been made by a team of senior members of the committee staff, officially under the authority of Niels Munk Plum. It is, however, only fair to stress that by far the greater part of the work has been done by G. M. Idorn.

It stems from the very nature of a compilatory work that we have been forced to present only very brief and probably often rather inadequate summaries of the opinions and findings of the various authors, and we beg to apologize for all imperfections.

It is a special pleasure to thank Mr. Jørn Jessing, who has carried the editorial responsibilities and Mr. Gunnar Larsen from the Geological Survey of Denmark for the contribution on investigations of flint and cherts, etc.

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Discussion

Tor Hagerman

The Swedish Committee on Aggregates was set up for the purpose of assessing the suitability of various types of rocks as aggregates in concrete. The investigations conducted by the Committee have been carried on since 1954. The object of these investigations is to find out whether and to what extent harmful effects of a chemical nature have been produced by natural gravel materials as well as by crushed stone.

In particular, the Committee is dealing with two subjects, first, the types of damage caused by the presence of pyritic minerals in the aggregate, and second, the types of damage due to reactions between alkalies and silica.

Investigations of Types of Damage Caused by Pyritic Minerals

These investigations were started immediately after the formation of the Swedish Committee on Aggregates. They were urgent because large-scale construction projects were in process of execution in regions where such cases of damage had previously been observed. Aggregates which had varying contents of pyritic minerals (magnetic pyrites, i.e., pyrrhotite, and pyrites) as well as rocks which were completely free from such minerals were used in making concrete beams, which were stored in different ways, indoors as well as outdoors. Even after a short time (8 months), those beams which had been tested at a rate accelerated by heat treatment showed unmistakable signs of deterioration in the form of swellings and deflections around strongly expanding portions situated in the interior, frequently in conjunction with rusting. These observations were made in the cases where the aggregates had relatively high pyrite contents, which ranged from about 15 to 20 percent. Subsequently, all beams were stored outdoors, and then—after about 5 yr—it was found that, irrespective of the method of previous storage, many of those beams which contained pyrite had totally disintegrated. On the other hand, the comparison test specimens, made with granite aggregate which was practically free from pyrite, did not exhibit any signs of defects.

Investigations of Types of Damage Due to Reactions Between Alkalies and Silica in Swedish Aggregates

These investigations were made, first, by means of petrographic examination, and second, by the aid of chemical determination in accordance with ASTM designation C 289–54 T and as mortar-bar expansion tests in conformity with ASTM Designation C 227–52 T.

The investigations (about 40 in all) dealt with gravel and rocks. They were largely carried out on aggregate materials belonging to the Caledonian series, which originated from mountainous regions of Sweden.

Some investigations made in Denmark have thoroughly clarified the types of damage, the expansion effects, etc., due to flint concretions, or the like, which are found in chalk deposits. Such chalk flint from Scania, in south Sweden, has also distinctly shown harmful expansion in the investigations under consideration. It may be mentioned as an example that an admixture of 5 percent of flint added to a granitic material resulted in an expansion of slightly over 0.3 percent after 12 months. The alkali content of the cement was 1.2 percent of equivalent Na_2O.

It is suspected that some types of gravel from mountainous regions can likewise cause harmful effects. These gravel types can contain, among other things, quartzite, sparagmite, and phyllite.

Field observations have revealed some cases of damage to concrete in which the reactions between alkalies and silica were regarded as a possible cause of damage. Up to now, however, it has not been possible to verify this assumption.

Chemical examination of aggregate materials has in several cases indicated that the amount of silica (S_c) dissolved out of quartzites and similar rocks is so great that the occurrence of harmful expansion is to be expected. It is true that manifest expansion of bars made with such aggregate has been observed in some cases where the cement had a high alkali content, but no reliable signs of an alkali reaction were to be detected.

The bars made with aggregates which were obtained from rock types belonging to the Caledonian series did not exhibit any cracks or any formation of an alkali-silica gel. Thus, it has not yet been found out what caused the expansion referred to above. It is known that expansion phenomena whose causes have not been elucidated had also been met with in Canada. Unfortunately, the available data on the types of rocks used in Canada are not sufficient to permit any conclusions by analogy as to the observations made in Canada and in Sweden.

Discussion

W. C. Hansen

The authors of the paper "Chemical Reactions Involving Aggregate" make the following statement: "One major problem, which in the opinion of the writers is not clarified sufficiently, is the fundamental nature of the chemical reactions between alkalies and reactive aggregates and the nature of their mechanical effects." The following is an attempt to offer a solution to this problem.

In my 1944 paper [1],[1] I stated "Since the alkali silicates must form in the space originally occupied by the silica from which they formed, and since these silicates must occupy a greater volume than that occupied by the silica alone, they would tend to exert pressure against the confining paste which would be augmented by the hydrostatic pressure."

In 1947, Vivian [2] stated "A series of changes in the properties of the opal particles can be observed as they react and absorb water. Initially, opal particles are hard but, as they react with alkalies, they soften gradually and swell and eventually become jelly-like." He also states "Expansion continues as long as the reaction product can absorb water and retain the property of rigidity characteristic of a gel. Since the gel exerts both hydrostatic and directional pressures, the reaction product not only expands in the plane of the crack through the mortar but also at right angles to it."

L. S. Brown [3] states "As observed in the variety of instances illustrated, damage by alkali-aggregate reaction appears to be effected by direct enlargement of the affected aggregate unit."

These statements lead to the conclusion that the investigators visualized solid opal reacting as a solid with OH^-, Na^+, and K^+ ions and H_2O molecules to form a solid reaction product. Jeffery [4] called this type of reaction a solid-state reaction.

Studies with glasses support the concept of this solid-state reaction. Marboe and Weyl [5] state the following regarding cesium glass: "If such a glass is stored in a desiccator over $CaCl_2$, it is exposed to an atmosphere which has a finite but a very low partial pressure of H_2O. Each H_2O molecule hitting the surface of the glass must be given sufficient time to migrate into the interior in the form of OH^- ions. If the H_2O concentration in the atmosphere is higher, hydrated alkali silicates are formed. Within three to four months, a cesium disilicate glass took up approximately 15 percent water and changed into a plastic translucent hydrate."

In 1955, Gaskin, Jones, and Vivian [6] placed opal and quartz-containing aggregates in a cement paste containing radioactive sodium. The hardened pastes were ground to expose the aggregate particles, and the surfaces were autoradiographed. They found a considerable accumulation of sodium throughout the opal particles after storage at room temperature for only one week.

McConnell, Mielenz, Holland, and Greene [7] found the following reactive components in aggregates: opal, chalcedony, volcanic glass, devitrified glass, and tridymite. Vivian [8] found that tetramethyl ammonium hydroxide as well as NaOH and KOH reacted with opal and produced expansion in mortar bars. In this paper, the discussion will be limited to opal and NaOH, but it should be understood that what is said regarding opal and NaOH applies in a general way to other reactive materials and other relatively strong alkalies.

It seems that the work in this field clearly shows that OH^- and Na^+ ions migrate into opal and form solid alkali silicates. As these products imbibe water and tend to become jellylike, one may question whether or not they should be classed as solids. However, the pieces of opal have been transformed from hard solids to jellylike bodies without having formed what is usually visualized as a solution.

In my paper, I suggested that the hardened cement paste might act as a semipermeable membrane to permit concentrated solutions of alkali silicates to form and exert hydrostatic pressure. Vivian and Brown were of the opinion that the solid state reaction cracked the concrete before such solutions were formed. According to Vivian, the concrete would be cracked sufficiently to permit the product to flow away from the site of the opal grain when the product became less rigid than the rigidity normally associated with a gel.

It is well known that the various forms of silica, quartz, opal, etc., are not generally attacked by acids and solutions of neutral salts but are attacked by alkaline solutions. This fact, of course, leads to the conclusion that OH^- ions are the units which attack the silica. As these ions penetrate the lattice of the silica, positive ions must accompany them to maintain electrical neutrality. From the standpoint of mass action, it is obvious that the rate of attack will vary with the concentration of the OH^- ions in the liquid surrounding the particle of silica. The work by Vivian with radioactive sodium indicates that Na^+ and OH^- ions migrate some distance into a grain of opal embedded in a hardened cement paste before the opal is changed to any marked degree.

Terms such as alkalic silica gel, alkali-silica complex, lime-alkali-silica complex, and silica gel have been used in referring to reaction products formed by opal in cement pastes. It seems unquestionable that opal cannot produce any expansion in cement pastes until the SiO_2 groups of the opal have been converted to SiO_3 groups. It is conceivable that some particles of SiO_2 may be more or less suspended in the reaction products, but they would have no ability to produce expansions, and, accordingly, one need not attempt to use language which would include such particles. Since there must be a chemical reaction between the opal, OH^- ions, and certain cations to form the SiO_3 groups which are associated with the silicates, it seems desirable to refer to these reaction products as silicates.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Let us review briefly some of our knowledge of alkali silicates. Suppose 140 g of crystalline $Na_2SiO_3 \cdot H_2O$ is placed in a beaker in a desiccator over pure water. The crystals will take up water to form a jellylike mass which will become less and less viscous until it resembles water containing a little sediment. What happens is that the sodium silicate goes into solution and hydrolyzes to form relatively insoluble hydrated silica or silicic acid and a dilute solution of NaOH.

The 140 g of $Na_2SiO_3 \cdot H_2O$ contained the equivalent of 80 g of NaOH. If we substitute 80 g of pellets of NaOH for the crystals of $Na_2SiO_3 \cdot H_2O$, the pellets will take up water to form a similar jellylike mass which will become less and less viscous until it resembles water. In this case, there will be no sediment in the beaker. In each case, we have prepared a dilute solution of NaOH. By using large containers and sufficient water, one can prepare infinitely dilute solutions of NaOH from these two compounds, and these could give rise to large hydrostatic pressures.

Suppose we placed either a quantity of crystalline $3CaO \cdot 2SiO_2 \cdot 3H_2O$ or of $Ca(OH)_2$ in the beaker. It would take very careful measurements to observe the imbibition of water by either of these products whereas the imbibition of water by the $Na_2SiO_3 \cdot H_2O$ and NaOH would be readily observed. The $3CaO \cdot 2SiO_2 \cdot 3H_2O$ would eventually hydrolyze into hydrated SiO_2 and an infinitely dilute solution of $Ca(OH)_2$, and the $Ca(OH)_2$ would eventually form an infinitely dilute solution. However, the rates of these reactions are extremely slow because of the relatively insoluble natures of $3CaO \cdot 2SiO_2 \cdot 3H_2O$ and $Ca(OH)_2$.

In the terms used by Powers and Steinour [9], the crystalline $Na_2SiO_3 \cdot H_2O$ would be classed as an unlimited swelling gel and the crystalline $3CaO \cdot 2SiO_2 \cdot 3H_2O$ as a limited swelling gel. According to Webster, a gel is a jellylike material formed by the coagulation of a colloidal liquid. If one accepts this definition of a gel, it may be inaccurate to refer to the reaction products of opal with alkali and calcium hydroxides as gels. Since the behaviors of the alkali and calcium silicates are so readily explained on the basis of solubilities, there appears to be no reason for thinking of them in terms of gels.

From the experiments described above, one sees that approximately equal hydrostatic pressures would be produced by 80 g of NaOH and by 140 g of $Na_2SiO_3 \cdot H_2O$. One can, therefore, arrive at the conclusion that the expansion produced by the alkali-aggregate reaction in a hardened cement paste is produced by the NaOH and that the aggregate plays a secondary role. On this basis, it may be concluded that the role of the aggregate is to concentrate the alkali into a few spots and change it into a form in which it can exert pressure by a reaction with water. How can NaOH and SiO_2 develop pressures in a hardened cement paste? They can react as follows:

$$Na^+ + OH^- + SiO_2 = NaHSiO_3 \tag{1}$$

$$Na^+ + OH^- + NaHSiO_3 = Na_2SiO_3 \cdot xH_2O \tag{2}$$

$$Na_2SiO_3 + \text{Water} = Na_2SiO_3 \cdot xH_2O \tag{3}$$

$$Na_2SiO_3 + SiO_2 + \text{Water} = Na_2H_2(SiO_3)_2 \cdot xH_2O \tag{4}$$

$$Na_2SiO_3 + nSiO_2 + \text{Water} = Na_2H_{2n}(SiO_3)_{n+1} \cdot xH_2O \tag{5}$$

One can visualize that, in reaction (1), an OH^- and an Na^+ ion penetrate the lattice of the grain of opal. As additional ions penetrate, they may form water molecules and molecules of Na_2SiO_3 which can imbibe water molecules from the hardened paste. As the $Na_2SiO_3 \cdot xH_2O$ imbibes more and more water, Na^+ and OH^- ions will be released to react with additional SiO_2 to produce a product such as $Na_2H_{2n}(SiO_3)_{n+1}$. The reaction indicated by eq (5) might be capable of continuing until an infinite amount of SiO_2 is converted to $Na_2H_{2n}(SiO_3)_{n+1}$ or until each silicate molecule contains only a trace of Na^+. However, the rate of this reaction will become too slow to be of concern to the cement technologist when some finite amount of SiO_2 has reacted. This amount, of course, will vary with the alkali content of the specimen under study.

It is well to digress here to point out that the liquid phase of the cement paste contains Ca^{2+} as well as Na^+ ions. Hence, as the Na^+ ions are migrating into the grain of opal, Ca^{2+} ions will accompany them. However, because of the low solubility of $Ca(OH)_2$ in solutions of NaOH, the number of Ca^{2+} ions available for migration into the opal is very small compared to the number of the Na^+ ions. However, the Ca^{2+} ions that do migrate into the grain of opal will produce an insoluble calcium silicate which will occupy more volume than that of the opal from which it was formed. In other words, any cation that migrates into the grain of opal will cause an expansion regardless of the solubility of the product. Attention was recently called to this fact [10].

According to Vail [11], crystalline compounds of the compositions $Na_2SiO_3 \cdot 2H_2O$, $Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ are known. Hence, highly hydrated metasilicates could be produced by the reaction of eq (2). The densities of these compounds are, respectively, 1.749, 1.807, and 1.646.

When 1 mole of SiO_2 reacts to form 1 mole of $Na_2SiO_3 \cdot 9H_2O$, 60.1 g of SiO_2 with a density of 2.3 yields 284 g of silicate with a density of 1.65; that is, 26.1 cc of SiO_2 forms 172 cc of silicate.

This reaction can be expressed in terms of dimensional change by taking the cube roots of 26.1 and 172, which are 2.9 and 5.6, respectively. Hence, if a particle of opal could be transformed (without any of it going into solution) into solid $Na_2SiO_3{\cdot}9H_2O$, the dimensions of the particle would be approximately doubled. The results of this calculation certainly lend support to the conclusion of Vivian and Brown that the concrete is cracked before the sodium silicate becomes fluid. However, one must remember that hardened cement paste can yield to pressure without cracking and that reactive particles may vary markedly in size. A small particle may have to undergo a greater percentage enlargement than a larger one before the paste ceases to yield to it. Hence, it may be that, in some cases, the alkali silicate develops a fairly high degree of fluidity before the paste cracks.

Vivian [12a] performed an experiment in which 18–52 mesh opal was used in a mortar made with a cement containing alkalies equivalent to 0.98 percent. At the age of 224 days, the expansions were approximately as follows:

Ratio Opal/ Na_2O	Expansion
	Percent
2	0.6
5	1.3
10	1.6
20	1.2
40	.6
60	.2
80	.0

It is well known that SiO_3 ions in silicic acid are highly polymerized and that the degree of polymerization can be decreased by additions of alkali hydroxides. The extent to which the hardened cement paste can confine the alkali silicate to the reaction site will depend upon the degree to which the SiO_3 ions are depolymerized when the alkali silicate assumes the properties of a liquid. Verbeck and Gramlich [13] have shown that sodium silicate can diffuse through hardened cement pastes having water-cement ratios of 0.55 and above.

Hence, it seems that, in specimens with the same water-cement ratio, the expansions will be controlled by one of two factors. When the specimen contains a small amount of opal with respect to Na_2O, all of the opal will be converted to a silicate with a composition in the range Na_2SiO_3 and $Na_2H_{2n}(SiO_3)_{n+1}$. When n is either zero or a small number, the volume change probably ends when the silicate reaches a certain fluidity. The specimen may or may not have developed cracks before this fluidity was reached. When n is a larger number, the silicate may never become fluid because of the lack of NaOH. That is, this product can be visualized as largely hydrated silica.

When the specimen contains a large amount of opal with respect to the Na_2O content, opal will react until the silicate has the composition $Na_2H_{2n}(SiO_3)_{n+1}$ in which n is a relatively large number. This product will be a solid that cannot imbibe water and cannot generate NaOH for reaction with the unreacted opal. To be correct, one should say that the rates of imbibition of water and of splitting off NaOH have become too low to be significant in the expansion of the specimen. Gel exudations from concrete have been analyzed by a number of investigators, and, according to Vivian [12b], the $Na_2O{:}SiO_2$ ratios have ranged from 1:2 to 1:16.

Vivian obtained maximum expansion at a ratio of $1Na_2O$ to $10SiO_2$. In accordance with eq (5), the composition of this product would be $Na_2H_{18}(SiO_3)_{10}{\cdot}xH_2O$ or $Na_2SiO_3{\cdot}yH_2O+H_{18}(SiO_3)_9{\cdot}yH_2O$. The ratio of Na_2O to SiO_2 by weight is 60 to 620. This is approximately 10 percent of Na_2O by weight of silica. It seems reasonable to believe that reaction (5) might convert all of the SiO_2 to SiO_3 in this product at a fairly rapid rate.

A high expansion was obtained at a ratio of $1Na_2O$ to $20SiO_2$. The product might have had the composition $Na_2SiO_3{\cdot}yH_2O+H_{38}(SiO_3)_{19}{\cdot}yH_2O$. In this, the ratio of Na_2O to SiO_2 is 60 to 1240. This is approximately 5 percent Na_2O by weight of SiO_2.

The rate of reaction (5) is controlled by the rate at which water can reach the reaction site. It seems entirely possible that, where the specimens are exposed only to water vapor, the rate of this reaction would become very low because of the slowness with which water could reach the reaction site.

Suppose, for the sake of argument, that the reaction stops when the molecular ratio of $SiO_2{:}Na_2O$ is greater than 20:1, that the composition of the reaction product is $Na_2H_{38}(SiO_3)_{20}$ and that the volume of the reaction product is equal to the sum of the volumes of the reactants. We then have

$$\begin{array}{ccccccc} 2NaOH & + & 20SiO_2 & + & 18H_2O & = & Na_2H_{38}(SiO_3)_{20}. \\ 36.6 & + & 522 & + & 324 & = & 882.6 \end{array}$$

The cube roots of 522 and 883 are approximately 8.0 and 9.9. The dimensional changes of any particle are then about 24 percent; whereas, for the production of $Na_2SiO_3{\cdot}9H_2O$, they are about 100 percent. In the case of $Na_2H_{38}(SiO_3)_{20}$, it was assumed that its volume equalled the sum of the volumes of the reactants. Actually, its volume would be somewhat less than this, and, accordingly, the dimensional changes would be less than 24 percent.

The expansion per particle when the ratio of $SiO_2{:}Na_2O$ is 80:1 would then be approximately as follows:

$$\begin{array}{ccccccccc} 2NaOH & + & 80SiO_2 & + & 18H_2O & = & Na_2H_{38}(SiO_3)_{20} & + & 60SiO_2 \\ 36.6 & + & 2088 & + & 324 & = & 883.6 & + & 1566 \\ & & & & & & & & =2448.6. \end{array}$$

The cube roots of 2088 and 2449 are approximately 12.7 and 13.5. In this case, the dimensional expansion of an opal particle is only 6 percent.

When the opal to Na_2O ratio exceeds 20:1 (such as 40:1), one half of the particle would expand linearly about 24 percent, but the other half would not expand at all. Hence, the overall expansion of the particle would only be about 12 percent. One can explain easily that, for a given amount of Na_2O, the expansions would increase with increasing amounts of opal up to some maximum because of the increase in the amount of alkali silicate produced. However, one might expect the expansions to remain at this maximum as the quantity of opal reached and exceeded some value at which the rate of reaction (5) became very low.

The point that must be remembered in order to understand results such as those obtained by Vivian is that we are dealing with a solid-state reaction. As pointed out in the introduction, Vivian described how opal particles change from solids to jellylike particles. I [14] observed the same behavior for particles of commercial "silica-gel" when used as an aggregate. These observations seem to demonstrate unquestionably that grains of opal, except possibly extremely fine grains, do not form fluid alkali silicates until long after the cement paste has hardened.

The reaction of Na^+ and OH^- ions with opal must begin almost as soon as the concrete is made. Since this is a solid-state reaction, the grains of opal expand during the period when the cement paste is plastic as well as later. For some time after the paste becomes rigid, the paste is able to yield to the pressure exerted by the opal reaction. All the expansions of the opal particles that occur during this period and periods preceding setting do not result in any expansion of the concrete specimen. The amount of reaction of opal with alkali that occurs during these periods increases with increases in the surface area of the opal particles.

As the ratio of SiO_2 to Na_2O increases, the ability to imbibe water shown by the product produced as the Na^+ and OH^- ions migrate into the grain of opal decreases until the rate of imbibition becomes insignificant from the standpoint of the expansion of concrete. One can visualize that these particles of opal that have partially reacted with NaOH will take up Ca^{2+} ions and molecules of water at very slow rates for long periods of time and might, accordingly, tend to produce expansions at extremely slow rates.

Powers and Steinour [9] attempted to explain what they called safe alkali-aggregate reactions such as shown by Vivian when the $Na_2O:SiO_2$ ratio was 1:80 on the basis of approximately half of the SiO_2 escaping from the reaction site and being converted to calcium silicate. Their explanation ignores the experimental evidence presented by Vivian as to the manner in which opal reacts in mortar bars.

Very finely divided opal has been suggested as a pozzolanic material for preventing expansion when reactive aggregates are used with high-alkali cements. It seems that an extremely fine opal might react with the alkali hydroxide so rapidly that it would be converted to a calcium silicate with the release of the alkali hydroxide while the cement paste was still plastic. In that event, the alkali hydroxide would be available to react with the aggregate, and the pozzolanic material would be ineffective in preventing expansion. It appears, therefore, that the most effective pozzolans may not necessarily be the finest.

McCoy and Caldwell [15] suggested that it might be possible to inhibit the reaction of opal with NaOH by adding certain compounds to the cement. They found that lithium salts were effective in decreasing the expansion in certain mortars. However, in general, the additions of lithium salts did not eliminate expansion. For example, the following percentage expansions at 12 weeks were obtained with 1:2 Ottawa sand mortar with 0 and 2.5 percent of opal: No opal—0.036; no inhibitor—0.812; 0.5 percent of Li_2CO_3—0.505; and 1.0 percent of Li_2CO_3—0.073.

It appears from limited information in the literature that lithium forms relatively insoluble and only slightly hydrated silicates. For example, according to Mellor [16], Vesterberg prepared $Li_2SiO_3 \cdot H_2O$ by treating a solution of sodium metasilicate with solutions of lithium salts. The addition of lithium ions to a mortar containing opal would, therefore, tend to convert the opal into a product that would have little, if any, tendency to imbibe water.

In a recent paper [10], I suggested that lithium and barium salts would decrease the expansion caused by the alkali-aggregate reaction by converting the opal to insoluble silicates.

Since the rate of alkali-aggregate reaction is a function of the OH^- ion concentration, any salt that would not decrease this concentration should not influence the rate. Hence, since LiOH and $Ba(OH)_2$ are relatively soluble, their ions could be expected to migrate into the grains of opal along with the Na^+. The relatively insoluble $Ca(OH)_2$ would furnish a few ions to migrate along with the other ions. Hence, as pointed out earlier, one can visualize that a small amount of insoluble calcium silicate is produced as soluble sodium silicate is being produced. In the case of Li^+ and Ba^{2+} ions, relatively large amounts of insoluble lithium and barium silicates should be produced as the sodium silicate is being produced. Since they are insoluble salts, they should replace the Na^+ ions in the silicates so that, if sufficient amounts of either Li^+ or Ba^{2+} ions were present to react with all of the opal, there would be no sodium silicate in the reaction product, and the Na^+ ions would be free to migrate back into the cement paste.

If the Li and Ba silicates formed after the cement paste became rigid and formed in the space occupied by the opal, they should cause some expansion. However, being insoluble salts, they would not have the power of sodium silicate to imbibe water and produce hydrostatic pressures.

According to Mellor [16, p. 361], LeChatelier obtained a reaction between colloidal silica and a solution of $Ba(OH)_2$. He prepared $BaSiO_3 \cdot 6H_2O$ by allowing Ba^{2+} ions to diffuse into a solution of sodium metasilicate.

Two questions that have been discussed by several investigators are as follows:

(1.) Is the hardened cement paste impermeable to silicate ions and molecules or do calcium-alkali-silicate membranes form?

(2.) What part does hydrostatic pressure play in developing expansions?

Since Vivian has shown that the grain of opal expands more or less as a solid and produces expansion before the product becomes fluid enough to have any possibility of diffusing from the reaction site, the answers to these questions are not particularly relevant to an understanding of the chemical reactions involved when alkali reacts with opal in a cement paste.

In my discussion [14] of Brown's paper, I argued that grains of opal that appeared to be solids might, in reality, be extremely viscous liquids and, accordingly, be exerting hydrostatic pressure. Regardless of when the reaction product passes from the solid to the liquid state and regardless of whether or not a calcium-alkali-silicate membrane is produced, the fundamental nature of the alkali aggregate is illustrated in eq (1) to (5). It seems that, from Vivian's work, there can be no question that part of the expansion is produced while the grain of opal is solid and that a large amount of expansion can occur before the silicate molecules will be depolymerized sufficiently to migrate from the reaction site. In the case of large amounts of opal, the silicate molecules probably never become depolymerized to this extent.

It seems that some investigators and writers have failed to realize that Vivian was stating a fact when he said "Initially, opal particles are hard but, as they react with alkalies, they soften gradually and swell and eventually become jelly-like." For example, it seems that Powers and Steinour could not have proposed a hypothesis for a "safe reaction" which required the migration of relatively large amounts of silica from the reaction site if they had recognized that expansion occurred while the opal was either a solid or a highly viscous liquid.

I do not wish to give the impression from this discussion that no problems remain in the field of chemical reactions between aggregates and components of the cement. However, I do feel that the fundamental nature of the alkali-aggregate reaction is understood.

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Discussion

T. C. Powers

Although the review of our hypothesis (Powers and Steinour, 1955) on the alkali-aggregate reaction in the paper on "Chemical Reactions Involving Aggregate" was quite satisfactory, it seems advisable to present more explicitly some aspects of the hypotheses that are involved in Dr. Hansen's discussion [supra]. Dr. Hansen refers to the second of our two papers, but it is in the first paper, which was issued together with the second as PCA Research Department Bulletin No. 55, that we gave the results of our study of the questions dealt with by Dr. Hansen. Perhaps this accounts for the unfortunate misunderstanding reflected in the following quotations from Dr. Hansen's discussion.

Near the close of his discussion, Dr. Hansen said, "It seems that some investigators and writers have failed to realize that Vivian was stating a fact when he said, 'Initially opal particles are hard, but as they react with alkalies, they soften gradually and swell and eventually become jelly-like. For example, it seems that Powers and Steinour could not have proposed a hypothesis for a "safe reaction" which required the migration of relatively large amounts of silica from the reaction site if they had recognized that expansion occurred while the opal was either a solid or a highly viscous liquid.' " In an earlier passage he said, with respect to our explanation of a safe alkali-aggregate reaction (one that does not cause expansion), "Their explanation ignores the experimental evidence presented by Vivian as to the manner in which opal reacts in mortar bars."

Since our hypothesis was derived mostly from data published by Vivian and his collaborators it can hardly be said with justice that Vivian's data were ignored. What we did conclude, in a summary of several pages of discussion of the mechanism of expansion in our first paper, is given by the following quotation (pages 511–12).

"We can conclude that swelling pressure able to cause concrete to dilate significantly beyond its original dimensions can be produced only by the gel of the unlimited-swelling type—the alkali-silica complex. If the alkali-silica complex is fluid, and if it is confined, pressure may be generated as described by Hansen, that is, it may be hydraulic (osmotic).[1] If the complex is solid, that is, still a solid reaction rim, pressure may be generated by the swelling of the rim, even though cracks or cavities are present that would relieve hydraulic pressure. If the reaction rim, though solid, is plastic, semi-hydraulic pressure could develop, the pressure being hydraulic to the degree that it is equal in all directions. The fundamental cause of swelling is the same in all cases—the entry of water into a region where the effect of a solute or of adsorption reduces its free energy.

"The foregoing explanation of the mechanism of producing swelling through cement-aggregate reaction is in agreement with some features of explanations previously advanced. It involves the same mechanism proposed by Hansen: the swelling is due to imbibition of water, as Hansen supposed, but it is not necessarily the result of hydraulic pressure maintained by a semi-permeable membrane. . . . Vivian, whose explanation is nearly the same as ours, concluded that no semi-permeable membrane is involved—that the expansion is due to swelling of solids only. We, on the other hand believe that Vivian's conclusion was influenced by his observations on small laboratory specimens. When cracks occur in such specimens, soft or fluid gels may exude to the surface without producing further swelling. In mass concrete, however, isolated cracks may fill with alkali-silicate solution, and therefore the soft gel or solution in such cracks may develop osmotic pressure, the concrete itself functioning as a semi-permeable membrane. However, all such swelling is likely to be of less consequence than that which will have occurred earlier, that is, the swelling that produces the cracks that later become osmotic pressure cells. Hence, we agree with Vivian that solid swelling is probably the primary cause of damage."

Finally, in the general summary of the first paper the following statement appears:

"Expansion is produced when the alkali-silica complex imbibes water. The initial, most damaging expansion probably occurs while the reaction product is still solid, though expansion may occur after the product becomes plastic or fluid, if the initially formed cracks have no outlets. The force is that of a swelling pressure or osmotic pressure (hydraulic), the two being fundamentally alike."

In our development of an explanation for an expansive reaction we made no attempt to give the stoichiometry of the reaction product because we could find no evidence that the stoichiometry of the product was determinable from data at hand, or was an important factor. The important point seemed to be that the products would have a relatively high solubility in water, whether or not enough water was present to form an actual solution in the ordinary sense. On page 509 of the first paper we said,

"Whether water is held in a liquid solution, a solid solution,[2] or a 'surface solution' [i.e., by adsorption,] an energy potential does exist between that water and free water, provided that the solution is not infinitely dilute or that the gel is not already water saturated. When equilibrium does not exist, the same kind of change will take place in each case—that is, free water will begin to enter the solution or the gel, thus diminishing the initial free energy potential.

"Hence to know that water will have a tendency to enter a given region we need only to establish that the water already in that region exhibits less free energy than the water outside; the particular mechanism by which the energy potential is created is a secondary matter. Conversely, when water is observed to move spontaneously from one region to another, we know that for some reason an energy potential exists."

It is thus seen to be a fact that we recognized experimental evidence showing that when an expansive reaction occurs, expansion usually occurs while the reaction product is in the solid, or a quasi-solid state. It is *not* true that we postulated that such a reaction would involve diffusion of the silicate away from the reaction site, but it seemed to Dr. Hansen that we did so, apparently because he admits for consideration neither the possibility of a reaction product different from any of those given in his five equations, nor the possibility of a reaction process that involves opal in a mature specimen and yet requires no expansion. He did not discuss the evidence presented in our papers that such a product and such a process does exist; instead he asserted that ". . . any cation that migrates into the grain of opal will cause an expansion regardless of the solubility of the product." Yet, the unique aspect of our hypothesis is the presentation of evidence contrary to this assertion, the description of a reaction process that requires no expansion, and the defining of conditions necessary for this process. I shall now present further evidence supporting the hypothesis, but first let us examine alternative explanations.

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[1] This refers to Dr. Hansen's original hypothesis, which he now seems to have abandoned.

[2] Or, in view of the ideas expressed in Dr. Hansen's present discussion, we might add, "held by solid-state reaction."

Explaining why pulverized opal caused no expansion, Vivian said, "It is assumed that the volume increase of -300 mesh particles is smaller than the volume of pore space in the hydrated cement contiguous to the particle surfaces." (However, in the same place he spoke also of ". . . other reactions akin to that of pozzolanas.") Hansen says all reactions occurring in an opal particle are expansive whether they involve lime or not, but "When the specimen contains a large amount of opal with respect to Na_2O content, opal will react until the silicate has the composition $Na_2H_{2n}(SiO_3)_{n+1}$ in which n is a relatively large number. This product will be a solid that cannot imbibe water and cannot generate NaOH for reaction with unreacted opal." In other words, the reaction stops, at least virtually, after enough reaction has occurred to raise n of the product to a sufficiently high value. He suggests that this value might be 20, and he calculates that when the total silica is 80 times the amount of alkali, the opal particles could not expand more than 6 percent before the reaction stopped. How this 6 percent expansion occurs without a corresponding expansion of the specimen is indicated by the statement, ". . . the grains of opal would expand during the period when the cement paste is plastic as well as later. For some time after the paste became rigid, the paste would be able to yield to the pressure exerted by the opal reaction. All the expansions that occurred during this period, and periods preceding setting, would not result in any expansion of the concrete specimen. The amount of reaction of opal with alkali that would occur during these periods would increase with increase in the surface area of the opal particles."

Vivian's supposition that the paste is able to absorb the expansion of small particles runs counter to what was revealed later about the size of pore spaces in hardened paste, if the absorption is supposed to involve pores; if it is supposed to to be a mechanical yielding, it runs counter to mechanical considerations, as will be shown later. We find evidence to support Hansen's view that a significant amount of an expansive reaction may occur before time of set, but the supposition that some expansion of opal particles after set could occur without dilating the specimen also is contrary to mechanical principles. We find no evidence to support the supposition that the reaction stops, even virtually, when the expansion stops. Experimental evidence that reaction continues will be given further on. Also, we find no experimental support for the statement made with reference to the calcium ion, that ". . . any cation that migrates into the opal will cause an expansion . . .". Evidence that this is not true has already appeared and more will be given below. I find no experimental evidence that an impervious reaction product unable to imbibe water is ever formed.

There is, however, an area of agreement common to Hansen's theory and ours that can be seen in figure 1. This curve gives the number of days required to reach about 90 percent of ultimate expansion, as a function of the opal content of the mortar. The data are from the same source as the data quoted by Hansen (see table in his discussion). The opal is in the form of $-18+52$ mesh particles; the alkali content of the cement is equivalent to 0.98 percent Na_2O. The graph is based on the expansive effect of reactions occurring after the first 20 hr. For the present purpose, we are mainly interested in the decrease in expansion period as opal contents rise higher than 2 percent of the volume of the mortar bar.

According to Hansen's hypothesis, expansion occurs until the ratio of silica to alkali reaches an upper limit beyond which the reaction virtually stops, the product having become impervious. Part of the reaction occurred while the mortar was plastic, and part afterward, the latter part being that which produces expansion. Or, since the reference length was that at about the age of 20 hr, we can say that part of the expansion occurred before the first measurement of length, and the rest afterward, the latter part being that represented in figure 1. The length of time during which expansion was observed was therefore determined by the fraction of the total reaction remaining to be completed after the initial length reading. This fraction depends on the total area of the opal particles presented to the alkali solution, the area in this case being directly proportional to the opal content of the specimen.

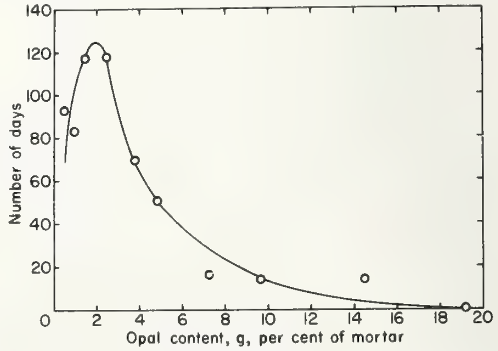

FIGURE 1. *Time required to reach 90 percent of ultimate expansion.*

Data from same source as in table 2.

At some sufficiently high surface area, all the reaction could be completed before the first length measurement. Evidently, this condition was found when the opal content reached about 20 percent of the volume of the bar.

Our hypothesis agrees with this interpretation to some degree. It recognizes that the reactions occurring before the paste sets play a highly important role, but beyond that ours differs radically from Hansen's. So far as the data of figure 1 are concerned, there is no obvious reason for preferring our hypothesis. The reason appears when such data as those shown in figure 2 are considered. This is a plot of expansion of mortar bars against elapsed time after molding, the time being expressed on a square-root scale as a convenient means of compressing the scale. Seven sets of mortar bars are represented, each containing the same amount of opal, namely 20 percent of the aggregate or 9.6 percent of the specimen; but each set of bars contained a different size of opal particle. The main point of interest is brought out by the data given in table 1 derived from figure 2. For each size of particle there was a period during which no expansion occurred. For the largest particle, the period was 12 days, for the −200 +300 mesh particles it was 115 days, and for the pulverized opal, −300 mesh, the period was apparently indefinitely long. Other data show that only when the ratio of opal surface area to alkali is low does the experimenter find expansion already under way at the time of the initial measurement. A successful hypothesis must take into account the various lengths of time that may elapse before expansion first begins.

Table 1. *Periods of nonexpansive reaction*

Opal content: 20 percent of aggregate; 9.6 percent of mortar

Alkali content of cement: Na_2O, 0.45 percent; K_2O, 0.81 percent

Data from: H. E. Vivian, Studies in cement-aggregate reaction *XIX* Australian J. Appl. Sci., 2, 488–494 (1951), table 4.

Sieve-size of opal BSS mesh	Period of nonexpansive reaction, days
−7+18	12
−18+52	12
−52+100	25
−100+150	80
−150+200	105
−200+300	115
−300	Indefinite

We can hardly conclude, with figure 2 before us, that a period of no expansion is necessarily a period of no reaction. Curve 2 of figure 2, representing coarse particles of opal, shows that expansion was going on during the period of no expansion by finer particles, curves 4, 5, and 6; yet it isn't conceivable that fine particles could remain inert while coarse particles of the same material, and initially in the same environment, reacted and expanded. There seems to be no way to explain the various periods of no expansion in terms of Hansen's five chemical reactions, and the formation of an impervious, high-silica product, without adopting fantastic assumptions to the effect that a once impervious product later becomes pervious, and that this event is later the smaller the opal particle.

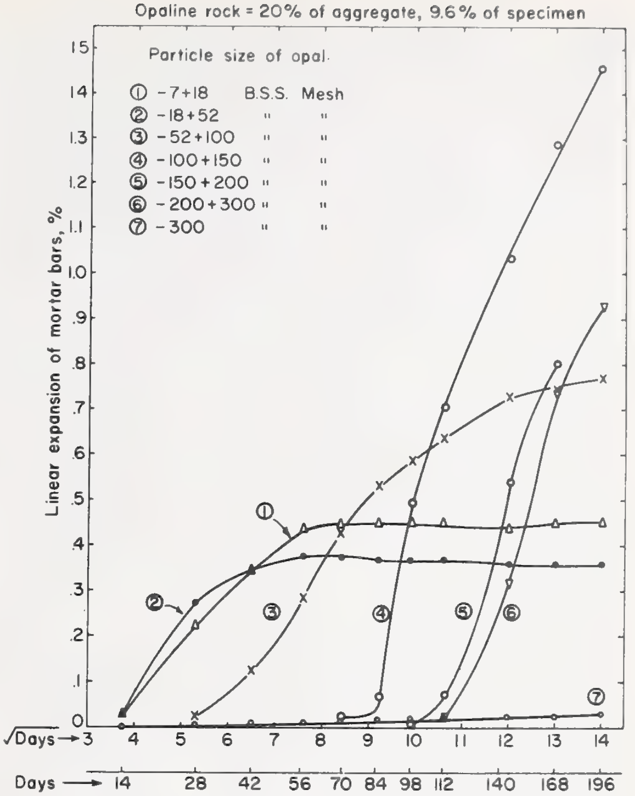

Figure 2. *Nonexpansive and expansive periods as functions of particle size.*

Data from source given in table 1.

The periods of no expansion discussed above are what we called periods of safe reaction. The nature of the safe reaction becomes clear when one takes into account, as we did, the effect of the initial reaction on the composition of the liquid phase in the mortar bar, using Kalousek's data. One finds that the alkali content may become so depleted by the initial superficial reaction with opal particles that the ratio of adsorbed calcium to adsorbed alkali quickly rises to a level that gives a lime-alkali-silica complex that is pervious but cannot expand. Presumably, when the initial alkali concentration is high, the first reactions with silica produce an expansive product; but if the silica surface area is high enough, the layer of this product is very thin, and as the alkali concentration falls, calcium ion concentration rises, and the thin layer is converted to a nonswelling calcium-alkali-silica complex, all before the first time the length of the specimen is measured. The lime-bearing product may then continue to be formed, even in a well-hardened specimen, as long as the calcium ion concentration outside the opal particle remains high enough. For example, during the 115 days of nonexpansive reaction, the −200+300 mesh particles probably acquired a slowly ingrowing layer of nonexpansive reaction product.[3] We believe that the process is the same (although the *reaction* is not the same) as that by which water attacks cement particles and produces an ingrowing layer of hydrated cement, and at the same time causes no expansion. This process requires the outward transport of about half the product of reaction. Thus, it was in connection with this *safe* reaction that we postulated the outward diffusion of silica. The expansive reaction is expansive precisely because such a transfer of matter cannot take place before destructive expansion occurs. I have discussed the mechanics of this process, as it occurs in the hydration of cement, in a recent paper. (Journal of the PCA Research and Development Laboratories, Jan. 1961). The process is possible when the reaction product is a dense, limited-swelling, gel. It is not possible if the product is an unlimited-swelling gel, or if the product is noncolloidal.[4] The factors governing the conditions for the safe reaction, and the duration of the safe period, are fully discussed in our second paper.

Hansen expressed the view that the reaction of lime with sodium silicate releases *all* the alkali and thus may restore conditions for a high-alkali reaction, but Kalousek's data shows that this need not be so, and the behavior of bars as seen in figure 1 indicates that it is not so in this case; and the probable reason is that the reaction product has a very high specific surface area. Kalousek's data enabled us to deal quantitatively with the fraction of alkali released by the calcium reaction, and the fraction retained by the product of the reaction, presumably by adsorption. There need be no fear about using extremely fine opal powders, or other pozzolanic powders. The finer the powder, the less of it required, up to the point where the initial reaction consumes all the material.

Bennet and Vivian (1955) demonstrated that when enough pulverized opal was used, coarse particles could be present also without undergoing expansive reactions. This shows that we are not concerned with particle size per se, but with the control of the environment of reactive particles.

It may be that some persons will be inclined to explain figure 2 in terms of an assumption that some of the expansion of small particles is somehow "absorbed" by the matrix. Since this is a recurrent argument, it seems appropriate to deal with it here. The following analysis is probably not as rigorous as it might be, but it seems to be adequate for the present application

Consider a hollow sphere of concrete, this shape being chosen for simplicity. The radius of the outside surface is b, and that of the inside surface is a. The question is, how much will each surface be displaced radially when a pressure, p, is applied to the inside surface.

Assume that the material has virtually no tensile strength, and therefore develops radial cracks between segments of unstressed material when dilation occurs. Under this condition, the changes of radial length are equal, and therefore,

$$\frac{\Delta b}{b}=\alpha_1\frac{\Delta a}{a} \tag{1}$$

where $\alpha_1=a/b$, and Δb and Δa the changes of the two radii.

Now assume that the sphere offers elastic resistance to dilation. Using established formulas of mechanics, Pickett (1956) gave the following general expression for radial displacement, δ, of any point in the sphere at the distance r from the center.

$$\delta=\frac{pa^3}{Er^2}\left[\left(\frac{1-\mu}{2}\right)\left(\frac{b^3+2r^3}{b^3-a^3}\right)+\mu\left(\frac{b^3-r^3}{b^3-a^3}\right)\right] \tag{2}$$

E is Young's modulus and μ is Poisson's ratio of the concrete.

Letting $r=b$ and solving for δ gives the displacement of the outside surface, Δb, i.e.,

$$\frac{\Delta b}{b}=\frac{3p}{E}\left(\frac{a}{b}\right)^3\left[\left(\frac{1-\mu}{2}\right)\frac{1}{1-\left(\frac{a}{b}\right)^3}\right]. \tag{3}$$

Similarly, from $r=a$, the displacement of the inner surface, Δa, is obtained;

$$\frac{\Delta a}{a}=\frac{p}{E}\left(\frac{1-\mu}{2}\right)\left[\frac{1+2\left(\frac{a}{b}\right)^3}{1-\left(\frac{a}{b}\right)^3}\right]+\mu. \tag{4}$$

Letting $a/b=n$, and dividing eq (3) by eq (4) gives

$$\frac{\Delta b}{b}=\alpha_2\frac{\Delta a}{a} \tag{5}$$

where

$$\alpha_2=\frac{3n^3\left(\frac{1-\mu}{2}\right)\left(\frac{1}{1-n^3}\right)}{\frac{1-\mu}{2}\left(\frac{1+2n^3}{1-n^3}\right)+\mu}=\frac{3}{\frac{1}{n^3}(1+k)+(2-k)} \tag{6}$$

where $k=2\mu/(1-\mu)$.

Each opal particle in a mortar bar may be regarded as occupying a cavity, the radius of the cavity being the same as that of the particle. If v is the total volume of all the opal particles in the bar, and the particles are spherical and all the same size, the number of particles, N, is

$$N=\frac{v}{\frac{4}{3}\pi a^3}. \tag{7}$$

The amount of mortar per opal particle is V/N

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[3] The product might grow inward not only from the outer surface of a particle, but also from the boundaries of the pores of permeable opal particles. Such pores are probably very large as compared with pores in cement paste.

[4] Although cement-gel particles are somewhat crystalline, as may be also the particles of the Kalousek complexes, they are also colloidal.

where V is the volume of the bar, and thus the bar can be considered as being composed of N cubes of edge length $2b$ such that

$$8\,N\,b^3=V. \tag{8}$$

From (7) and (8),

$$\left(\frac{a}{b}\right)^3=\frac{3v}{V}\cdot\frac{2}{\pi}=\frac{6g}{\pi}=n^3 \qquad |0<g<0.523| \tag{9}$$

where g is the volume of opal per unit volume of the mortar bar. The maximum value of g, 0.523, is fixed by the chosen model.

Equation (1) can now be stated in terms of g; i.e.,

$$\frac{\Delta b}{b}=n\frac{\Delta a}{a}=\left(\frac{6g}{\pi}\right)^{\frac{1}{3}}\frac{\Delta a}{a} \tag{10}$$

and

$$\alpha_1=1.24g^{\frac{1}{3}}. \tag{11}$$

Similarly, eq (6) becomes

$$\alpha_2=\frac{3}{\frac{\pi}{6g}(1+k)+(2-k)}. \tag{12}$$

At this point, we may observe that in eqs (6), (10), (11), and (12), which give the relationship of the unit expansion of a mortar bar to the unit expansion of the opal particles it contains, the size of the particle does not appear; for a given percentage expansion of an opal particle, the effect on the bar depends on the total volume of the opal particles. This mechanical principle, plus the fact that expansion, when it occurs, begins while the particles are solid, shows that arguments based on a special effect of size are not tenable. Actually, as may be seen in figure 1, small particles may produce more expansion than an equal volume of larger particles. Vivian reported that, as might be expected, the smaller the particle the shorter the cracks. Because of this the cracks around small particles do not develop outlets to the exterior through which soft alkali-silica gel can escape until after a relatively high degree of expansion has occurred.

Arguments based on special size effects appear all the weaker when one considers how small an amount of opal can cause expansion, and especially how little expansion is required of the opal particles to produce observable effects when the opal content is upwards of 1 percent. This is considered further in the following paragraphs.

We shall now assume that all the cavities containing opal particles become expanded by pressure associated with the alkali-silica reaction, and that they expand simultaneously. Resistance to expansion is determined by the elastic properties of the mortar as indicated by Poisson's ratio, μ, and by the extent of crack development. If no cracks are produced the normal value of μ would apply, about 1/5. If the mortar deformed plastically, the value of μ would be 1/2, but studies of deformation under sustained stress show μ due to creep and plastic flow to be equal to or less than that due to short time loads. Therefore there is no factual basis for assuming that μ can exceed about 0.2. If cracks become so extensive that all resistance to expansion is lost, eq (11) applies. Therefore, calculations may be based on values of α_1 and α_2, the latter for $\mu=1/5$, or $k=1/2$.

Figure 3 gives plots of α_1 and α_2 vs. the opal contents of the bars, as calculated from eqs (11) and (12). From these functions it is possible to estimate the amount of expansion of the opal particles from the measured expansion of the bar. However, the result can be no better than an estimate, in most cases, because the degree of elastic resistance remaining at any given stage of expansion is not known. At a given opal content the value of α should fall between α_1 and α_2, if cracks are present. Probably, cracks appear at strains exceeding 0.05 percent. Under a normal tensile force, this amount of strain would correspond to a stress of 1,000 psi if the modulus of elasticity is 2 x 10^6 psi. From the measured expansion of the bar, the extent of cracking can be estimated on this basis.

An application to some of the Vivian data already cited is given in table 2. The first 3 columns give the opal-alkali relationships, and the 4th column the total expansion occurring

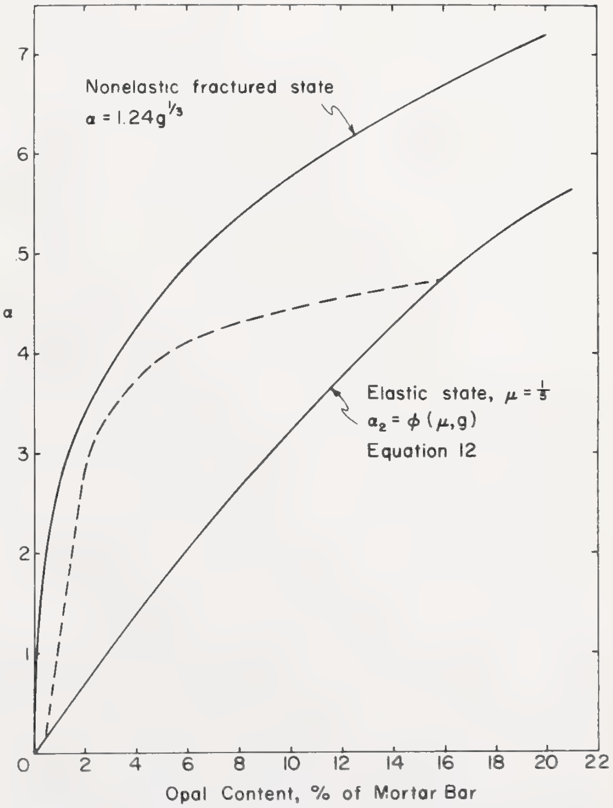

FIGURE 3. *The factor α of eqs (11) and (12) as functions of opal content of mortar bar.*

TABLE 2. *Calculations of expansion of −18 +52-mesh opal particles in mortar bars made with high-alkali cement*

$$\frac{\Delta a}{a} = \frac{1}{\alpha} \frac{\Delta b}{b}$$

Data from: Studies of cement-aggregate reaction: Bulletin 256 CSIRO Australia, p. 15, table 3.

1	2	3	4	5	6	7	8
Opal/ Na_2O	Opal content		Observed exp. 224th day	α (see text)	$\frac{1}{\alpha}$	$\frac{\Delta a}{a}$	Remarks
	Aggregate	Bar					
	Percent	*Percent*	*Percent*			*Percent*	
0.04	0.02	0.0096	0.0083 [a]	0.000036	28,000	230	Elastic.
.2	.10	.048	.0417 [a]	.0018	5,600	22	Elastic.
2	1.0	.48	.417 [a]	.025	40	17	Partly elastic.
4	2.0	.96	.83 [a]	.10	10	8.3	Partly elastic.
6	3.0	1.44	1.26 [a]	.18	5.6	7.0	Partly elastic.
10	5.0	2.4	1.62	.31	3.2	5.2	Partly elastic.
15	7.5	3.6	1.31	.36	2.8	3.8	Partly elastic.
20	10.0	4.8	1.03	.40	2.5	2.6	Partly elastic.
31	15.0	7.2	0.76	.42	2.4	1.8	Partly elastic.
41	20.0	9.6	0.52	.44	2.3	1.2	Partly elastic.
61	30.0	14.4	0.13	.46	2.2	0.3	Elastic.
82	40.0	19.2	0.00	.54	1.8	0.0	

[a] Values taken from a straight line through the data points. All the rest are results as reported by Vivian.

during 224 days of moist storage at room temperature. From the latter data, it was estimated that no cracks occurred in specimens containing less than 0.5 percent opal, also that cracks did not occur when the opal content exceeded 16 percent. At maximum expansion, found at an opal content of 2.4 percent the tensile strength was probably not over 15 percent of normal (Vivian, 1947), and therefore the value of α must have come close to α_1 at that value of g. The broken-line curve in figure 3 was drawn on the basis of these considerations as a reasonable guess of the locus of α vs. g for these particular data, and the values in table 2 are from this curve, except for the items marked "elastic", for which α_2 values were used.

The values in column 6 show the factor by which the unit linear expansion of the bar must be multiplied to obtain the unit linear expansion of an opal particle. For very small amounts of opal, less than 0.05 percent, this factor was found to be large, indicating that much of the expansion of the particles could be "absorbed" by elastic compression of the matrix. But for amounts of opal upwards of ½ percent, the factors are not large, partly because of cracks.

Column 7 shows the calculated linear increase of the opal particles corresponding to the measured increase in length of bar given in column 4. At peak expansion (1.6 percent), the estimated expansion of the opal particles is about 5 percent. If the expansion could have taken place elastically (no cracks) the particle expansion would have been about 11 percent. With 9.6 percent opal in the bar, the observed 0.52 percent expansion of the bar could be produced by only a 1.2 percent expansion of the particles, and with 19.2 percent opal there could have been virtually no expansion without measurable expansion of the bar.

Although it is obvious that various other sets of figures could have been arrived at by the general procedure followed above, it is also clear that any other set would tell the same story as to the magnitude of particles swelling.

These considerations also have significance with respect to Hansen's concepts of the expansive reaction. Referring to the bar containing 4.8 percent opal (SiO_2:Na_2O: :20:1), he says, "Suppose . . . the composition of the reaction product is $Na_2H_{38}(SiO_3)_{20}$ and that the volume of the hydration products is equal to the sum of the reactants." He then shows that, "The dimensional changes of any particle are then about 24 percent." It should be observed that this calculation includes only the water of constitution of the solid crystalline product, the x H_2O of his eq (5) not being included. The calculation therefore gives the least possible space the product could occupy before any additional water was taken into the site of the opal particle.

The prediction of a 24 percent linear increase of each cavity containing opal may be compared with the corresponding data in table 2, showing that the opal particles need expand only about 2.6 percent to account for the 1.03 percent expansion of the bar. It thus appears that the stoichiometries of the sodium silicates produced in the expansive reactions cannot be obtained directly from the total alkali and total reactive silica in the mortar bar.

There is much experimental evidence to support our conclusion that the alkali-aggregate reaction can produce either an expansive or a nonexpansive product, and that which of the two products will be produced depends upon the relative amounts of alkali and lime in the solutions outside the opal particles and on factors that control the rates of diffusion of water and ions.

Discussion

R. G. Pike, Donald Hubbard, and E. S. Newman

This paper on the chemical reactions involving aggregate has been very instructive, and we are particularly interested in the latter portion of the paper dealing with the alkali-aggregate reaction—specifically those remarks suggesting that calcium hydroxide may play an important role in the mechanism of alkali-aggregate expansion.

The importance of the role of calcium in the alkali-aggregate reaction is suggested by recent work in this laboratory on synthetic aggregates composed of binary silicate glasses. A paper has been submitted for publication (as Bull. 275) to the Highway Research Board in which the results of this work can be interpreted as an indication that the presence of a certain (unknown) concentration of calcium ions in solution is necessary to help in the formation of a semipermeable osmotic membrane about the individual aggregate grains before disruptive expansion can proceed.

In this investigation mortar bars were made and tested in accordance with ASTM Specification 227–52T, Tentative Method of Test for Potential Alkali Reactivity of Cement Aggregate Combinations, in which various glasses (reactive aggregates) replaced 6 percent of the nonreactive graded Ottawa sand.

One series of these glasses varied in composition from 50 percent Na_2O: 50 percent SiO_2 to 0 percent Na_2O: 100 percent SiO_2.

Figure 1 illustrates the expansions obtained with mortar bars made with these glasses using high-alumina cement and "pressure calcined" gypsum plaster. Since neither the cement nor the plaster contains any detectable alkali, these curves show that the soda-silica glass can supply the alkali necessary for expansion and can, at the same time, act as the reactive aggregate.

Figure 2 illustrates the same effect with a low-alkali (0.29 percent K_2O) portland cement, and it can be seen that the greatest expansion is caused by the glass composed of 15 percent Na_2O: 85 percent SiO_2.

This high expansion may be largely eliminated or greatly retarded by the substitution of pozzolan for part of the cement. This effect is illustrated in figure 3 for bars containing various amounts of pozzolan. In this series the bars containing no pozzolan expanded about 1.4 percent. This potential expansion was reduced to 0.2 percent by the substitution of 4 percent and to 0.02 percent

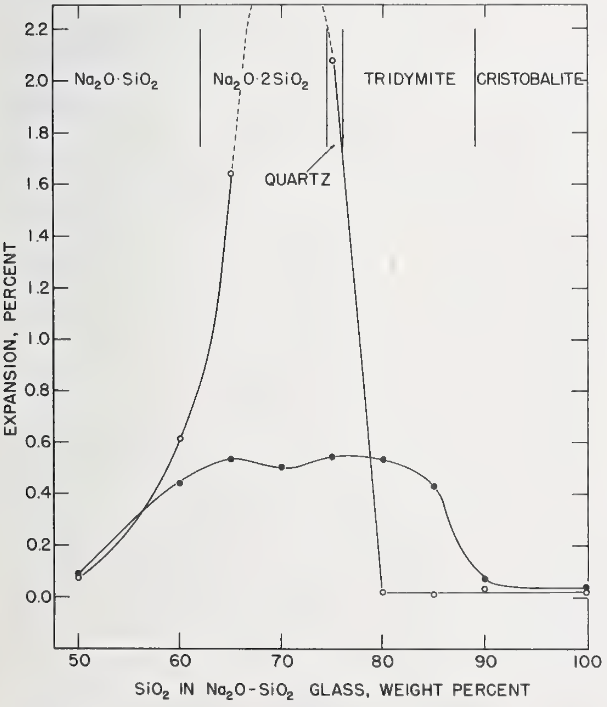

FIGURE 1. *Expansion of mortar bars containing a series of* Na_2O–SiO_2 *glasses.*

Stored over water at 100 °F.
● with high-alumina cement, aged 8 months.
○ with gypsum plaster; aged 2 months.
Also shown are the primary phase regions for the system Na_2O–SiO_2.

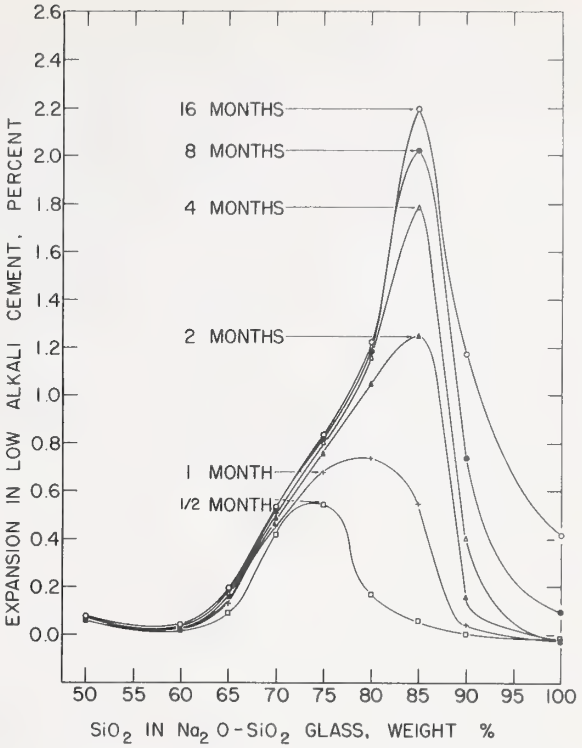

FIGURE 2. *Expansion of mortar bars containing a series of* Na_2O–SiO_2 *glasses in a low-alkali cement at various ages.*

Stored over water at 100 °F.

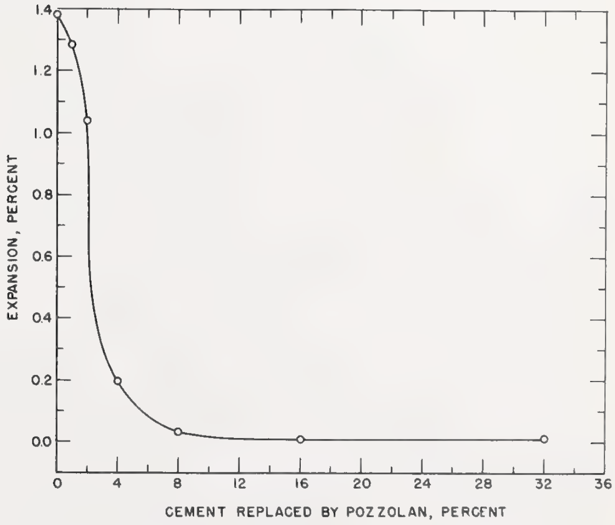

FIGURE 3. *Reduced expansion of mortar bars containing a 15-percent* Na_2O*:85-percent* SiO^2 *glass caused by partial replacement of the low-alkali cement with pozzolan (opal passing #325 sieve).*

Bars stored over water 4 months at 100 °F.

by the substitution of 16 and 32 percent of the cement by pozzolan.

It would appear from these results that the remarks of Conrow [1] and Mather [2] quoted by the authors are very apropos. The fact that there is less than one percent of total alkali in the mortar bar while about five times this much pozzolan is required to reduce the expansion to a low value suggests that direct reaction of the pozzolan with the alkali is not the only factor in reducing expansion.

The mechanism by which this pozzolan-calcium hydroxide reaction reduces expansion is not known, but we may speculate (since pozzolans are by definition materials which react with calcium hydroxide to form insoluble silicates and aluminates) that the reduced expansion is concerned with this traditional pozzolanic activity.

Kalousek [3] has suggested that precipitation of a soda-lime-silica gel about the reactive grain to form with the cement a semipermeable membrane is necessary for the harmful expansive reaction to occur. If such a membrane is necessary, any reaction which would tend to reduce the concentration of calcium ion in solution to a point where the membrane would not form should decrease expansion. Conversely, addition of materials which tend to increase the calcium ion concentration might be expected to increase expansion. Various investigators have shown that the addition of very small amounts of different materials can greatly increase or decrease the concentration of calcium ions in the liquid phase of setting portland cement pastes [4, 5, 6]. If the work of McCoy and Caldwell [7] is examined with this fact in mind, it appears that those materials which might be expected to cause an increase in the calcium ion concentration tend to increase expansion, and those which might be expected to cause a decrease in concentration or ionization of calcium tend to reduce expansion.

Some recent work by Lerch [8] on concrete specimens made with sand-gravels of the Kansas-Nebraska area is also of interest in regard to the role of lime in alkali-aggregate expansion. From an examination of his tables numbered 3 and 4 it appears that the cement having the highest percentage of C_3S (64.5 percent) and the lowest C_2S (10.0 percent) (that is, the cement which would be expected to release the most calcium) causes the greatest amount of cracking of the concrete specimens. Conversely, that cement with the lowest percentage of C_3S (25.0 percent) and the highest C_2S (48.0 percent) (that is, the cement which would be expected to release the least calcium) causes the least cracking. For those cements containing more than 0.57 percent of combined alkalies (either in the original cement or as added alkali) and falling between these two extreme values for C_3S and C_2S, there appears to be a fair correlation between the amount of C_3S and the cracking of the concrete.

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Discussion

John Lemish

The discussion presented below concerns the section on "Unidentified Cement-Aggregate Reactions" in which mention is made of concrete deterioration related to argillaceous dolomitic limestone aggregates. A considerable amount of research has been conducted on carbonate aggregate-cement reactions as part of the general study on the suitability of carbonate rocks as concrete aggregate, which inadvertently did not reach the authors in time to be incorporated in their paper. These reactions which occur in response to the alkaline environment of concrete are not typical alkali-aggregate reactions associated with siliceous aggregates such as opaline cherts, volcanic glasses, etc. The reactions are associated with certain carbonate aggregates whose service records indicate that deleterious performance in concrete has occurred. It is my purpose to review briefly carbonate-aggregate research conducted at Iowa State University and present some new data on the problem of carbonate aggregate-cement paste reactions.

Although a considerable amount of material has been published on concrete aggregates, few papers deal specifically with carbonate aggregates. One of the first papers on carbonate aggregate was written by Loughlin [1][1] in 1928. Other work by H. S. Sweet [2], B. Mather, et al. [3], and K. Mather [4] dealt directly with carbonate rocks, emphasizing the petrographic and physical aspects. Within the past 5 yr, however, the recognition that certain carbonate aggregates contribute to distress in concrete because of chemical reaction has led to participation in research by several other groups in the United States and Canada. Significant contributions have been made by Swenson and Gillot [5] on the Kingston aggregate in Canada, by Hadley and others under the direction of Verbeck at the Portland Cement Association Laboratories, and by Chaiken and Halstead [6] of the Bureau of Public Roads. Their work emphasizes the expansion of carbonate rocks in alkaline environments and especially the the reaction of carbonate minerals or "dedolomitization" with alkalies.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Because of direct correlation of poor service record of certain Iowa highways with the use of coarse carbonate aggregates from certain quarries, studies sponsored by the Iowa State Highway Commission were first begun in 1948 by Dorheim [7], who, by means of expansion tests on concrete bars, concluded that clay in limestone might be indicative of poor performance. Work was continued by Roy, et al. [8], who made a petrographic study of the Mississippian carbonate rocks which included those from LeGrand with a poor service record. Although there was no correlation of petrographic characteristics with service record, they observed that weathered aggregates with increased absorption were associated with distressed concrete.

In 1955 the research was renewed and investigation of Devonian rocks from the Glory quarry which produced rock with a notoriously poor service record led to a publication by Lemish, Rush, and Hiltrop [9] on the physical properties of the aggregates. They concluded that impure carbonate rocks characterized by high residue and clay content were poor aggregates, and they postulated that the pore-size distribution of the rock was important to serviceability. Examination of deteriorated concrete indicated that the softer matrix was carbonated and that impure coarse carbonate aggregates were characterized by reaction shells. Bisque and Lemish [10] also described the chemical properties of carbonate rocks as related to the durability of concrete, and found that reaction shells were silicified and selectively formed on aggregate containing clay, a high percentage of insoluble residue, high magnesium content, and higher amounts of silica. They reported a method of growing reaction shells on these impure carbonate rocks in silica-rich solutions at pH 12 and demonstrated that carbonate rocks reacted chemically in concrete environments.

Further study by Hiltrop and Lemish [11] conducted on the relationship of pore-size distribution and other rock properties to serviceability, led to the conclusion that pore-size distribution alone is not indicative of performance as an aggregate but that the presence of clay and the Ca/Mg ratio were definitely related to serviceability.

Continued study by Bisque and Lemish [12] demonstrated that reaction shells could be experimentally grown on impure aggregates in concrete bars and that shell growth in the instance of Glory aggregate was due to introduction of silica from the cement paste. Shells were also grown rapidly in cement-paste bars by Lemish [13] in an autoclave. Further studies [14] indicated that sodium and potassium were not introduced into the shell and that bars in which shells were grown had no increase in compressive strength accompanied by no excessive expansion. It was postulated by Bisque [15] and demonstrated by Hiltrop [16] by means of silicon tetrachloride and vaporous organic silicone compounds, that silica introduced into the rock could be stabilized or fixed by clay particles.

In recent unpublished research at Iowa State University under the direction of Lemish, Harwood [17] continued the study by measuring compositional variations in aggregate and cement resulting from carbonate aggregate-cement paste reactions. A series of different aggregates cut in the shape of a cube were placed in cement-paste bars of Type I cement (0.52 percent of alkali reported as Na_2O) and were soaked continuously in distilled water at 55 °C for 3 months. Two cubes of reactive Glory aggregate were similarly reacted with cements consisting of alite ($3CaO{\cdot}SiO_2$) and belite ($2CaO{\cdot}SiO_2$), respectively, at a pH 12 environment. Chemical analyses and X-ray studies were made on samples taken at specified intervals across the aggregate into the cement paste. Figure 1 gives the summary of silica behavior for different types of aggregates.

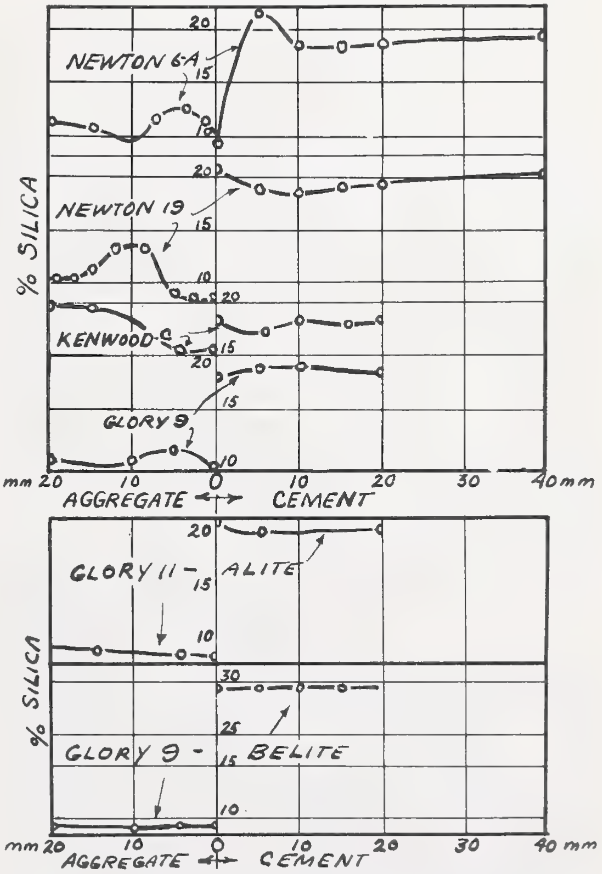

FIGURE 1. *Variation of silica content with distance from aggregate-cement paste interface.*

Silica shows variable behavior. In the case of the Glory aggregates which served as a basis for Bisque's work, silica increases in the reaction shell, and shows a drop in the cement paste. This behavior is also true for the Newton aggregates. Both aggregates can be characterized as dolomitic, lower-to-moderate insoluble residue types. In the Kenwood aggregate, a rock which behaves like the Kingston aggregate and is dolomitic with a high silica-rich residue, the reaction shell decreased in silica content and silica increased in adjacent cement paste. Regardless of how silica varies, a resistant silicified shell of amorphous silica results. In all cases magnesium migrates from the shell zone and some calcium migrates into the shell from the cement.

The cubes of Glory aggregate placed in alite and belite showed a behavior different from that when placed in portland cement. Silica was removed from the same type of aggregate which characteristically gained silica when placed in portland cement bars, indicating that alite and belite are not the source of silica in the shells.

X-ray data of the shell zone indicate quartz and dolomite decrease; calcite increases. In some instances some $Ca(OH)_2$ was found in the shell. In the immediately adjacent cement, the hydrated cement compounds showed a more disordered pattern.

Harwood's data suggest that silica migration is essentially an equilibrium reaction controlled by (1) the relative concentration of available silica in adjacent aggregate and cement, and (2) by the local pH environment. The dolomite-hydroxyl ion reaction (dedolomitization) explains the dolomite decrease and calcite increase in the shell. Some calcite could form through the introduced $Ca(OH)_2$ or Ca ions with CO_3 released during the reaction. Aggregates with low insoluble residue do not extract silica because they lack sites for silica precipitation or fixation and generally would have a good service record.

This latest research indicates that silica appears to move either way, and that all components of a carbonate aggregate are affected by alkali reaction. It emphasizes that several changes occur in the shell zone simultaneously. Shell formation does not mean a definite increase or decrease in silica content; it signifies the formation of amorphous silica.

Interesting as this data is, it must be pointed out that during all of Harwood's experiments it was assumed that the composition of the rocks was uniform and representative. One of the major problems in these studies is the experimental and quantitative controls needed to be positive of the direction of ion migration and compositional changes before and after an experiment. Since most of the quantitative methods of analysis are destructive, the initial composition must be assumed to be uniform and representative of similar materials.

In order to get around some of these experimental difficulties and to study silica behavior more accurately, Hiltrop [18] adapted a refluxing technique to measure silica more representatively. In an attempt to learn the form that the available silica or "silicate" is in and the conditions under which it migrates in and out of rocks, he applied the concept of "reactive" and "nonreactive" silica on the basis of the ammonium molybdate method [19] of silica determination and subsequent hydrofluoric acid treatment. After measuring the amount of silica in solution contributed by an aggregate by the ammonium molybdate method, it was found that HF treatment always increases the soluble silica present, indicating that more complex unavailable species of silicate are present. The immediately available species (probably monomeric silicate) was called molybdate "reactive" silica and the more complex HF-treated silicate, molybdate "nonreactive" silica.

Refluxing different deleterious aggregates in glass vessels at pH 12 produced varying amounts of reactive versus nonreactive silica. Hiltrop found that glass vessels produce 100 percent "reactive" silica in large amount. Cement pastes when refluxed in glass at the same conditions as the rocks produce very small amounts of total silica in solution, a large proportion of which is nonreactive and is accompanied by a coating of a calcium silicate compound on the walls of the reaction vessel.

This promising line of attack is being carried out in silica-free refluxing vessels, and it may show promise as a means of differentiating the potential reactivity of an aggregate in a manner more positive than present testing methods.

Summary

The research at Iowa State University raises more problems than answers. Research to date shows that the cement-aggregate reaction is selective and that dolomitic argillaceous carbonate rocks characterized by relatively high residues react with cement. All the components of the rock react to form a silicified "dedolomitized(?)"[2] shell. Silica can move in or out of an aggregate, and an attempt to study the form of the silica or "silicate" has led to the concept of "molybdate reactive" and "molybdate nonreactive" silicate.

Several problem areas remain where research needs to be done:

1. A need exists for more data on the behavior of Na and K in shell zones.
2. More data is needed on the behavior of silica and the conditions under which it migrates.
3. Data is required on sources of readily available silica in rock and cement.
4. More data on the true nature of carbonate rocks, especially mineralogical composition, texture, structure, and geological relationships.
5. The relation of carbonate aggregate-cement reactions to performance of concrete.

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[2] Magnesium may also come from a high-magnesium calcite.

6. Most important of all, knowledge of how alkali-induced reactions contribute to distress in concrete.

With regard to this last point, present information indicates that (excluding physical damage) distress can be produced by expansion, changes in the concrete or cement matrix, or a combination of both. If alkali reactions occur in the aggregate producing amorphous or some form of soluble silica which in turn may swell or expand because of osmotic processes, one can visualize that it is not the excessive amount of reactive silicate minerals which need be present, but the critical relationship between the size of the pore and the reactive silicate material present. A small amount of silica reacting in a small enough pore could cause enough confinement to produce expansion. This may be why some of our impure carbonate aggregates do not respond to the traditional alkali-reactivity tests which are being used.

One could also visualize that if silica is extracted from the cement, a gradual weakening of the concrete would result. Evidence that concrete in which carbonate aggregate-cement reactions have occurred does not gain strength during curing supports this possibility. Changes brought about in the cement during the reaction might even condition the concrete to later secondary changes which could cause additional expansion or deterioration.

Considerable progress is being made in carbonate-aggregate research, but the greatest gain this work has accomplished to date is the awareness that many types of reaction can and will occur when an aggregate is placed in concrete. The concept of cement-aggregate compatibility is more meaningful.

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Discussion

R. R. Hattiangadi and P. J. Jagus

Alkali-aggregate reactivity is known to have taken by far a very large proportion of the total toll of deterioration of concrete due to cement-aggregate reactions. There are, however, countries like Australia and Great Britain which are noted for complete absence of any notice of this reaction, although they have worked extensively on the very subject. For India, however, it cannot be said with any degree of confidence that there have been no cases of deterioration due to alkali-aggregate reactivity, as there do exist very large deposits of aggregates which are likely to contain potentially reactive minerals. The Deccan trap formations covering as much as 200,000 sq. miles in western India are known to contain reactive silica in the form of chalcedony, agates, zeolites, and glass. Besides, there are also known deposits of highly reactive traps and quartzites in the Kashmir area, and some reactive quartzites in the Delhi region.

Although there have been no cases of deterioration reported due to alkali-aggregate reactivity, it would be unwise to preclude its possibility merely on this consideration, because of the extended period of 8–12 yr. over which it could take place and the chances of its having gone unidentified due to want of scientific investigations.

As regards the part played by the level of alkali in cement, the two-decade-old contention regarding limiting the level at 0.6 percent Na_2O equivalent as a full and adequate safeguard against the possibility of the reactions could be looked upon with some doubt. Research work by Hanna and analysis of his and other data by D. O. Woolf in 1951 has brought out a concept of the alkali-silica ratio as governing the order of expansion more than the individual levels of the alkali and silica. Laboratory tests carried out at the Central Road Research Institute (India) have shown some validity of this statement. It could perhaps mean that the emphasis put exclusively on the level of the alkali may in the past have been overdrawn.

It may be mentioned that the current Indian standard specifications for portland cement do not contain any restrictive clauses regarding the maximum permissible limit for alkali content. However, utilizing the present-day knowledge of the subject, it would seem that potential reactivity could be avoided in areas of highly reactive aggregates by generally avoiding the use of high-alkali cements. In the absence of availability of cement with a sufficiently low alkali content, a recourse to the use of pozzolanic admixtures or pozzolan cements is indicated. With the extensive amount of research work that has been done all over the world on the subject, it cannot be denied that the mechanism of this reaction as understood even today carries a considerable element of hypothesis, if not of speculation. Even the precautionary measures recommended under some of the building codes and specifications on the basis of this work could perhaps be challengeable in respect of the safeguards assured by them.

I would like, therefore, only to emphasize that the authorities enforcing these codes should not have a tendency to run away with the mandates that are suggested in the codes, as research has made it amply clear that no one single variable, namely the level of the alkali or the reactive material, can cause harmful reactions. Due importance must be given to all scientific investigations and research and more particularly in considering the possibility of the reactions in the field to the study of single variables, their combinations, and the probability of any changes which may be brought about in their levels through peculiar environmental conditions before definite steps as safeguards against the dangers of these reactions are decided on.

Discussion

A. de Sousa Coutinho

In the very interesting and very well written report "Chemical Reactions Involving Aggregate", by P. Bredsdorff and co-authors, reference is made to a case of disintegration of mortar and concrete in sea water in the harbor of Leixões, Portugal.

The description of this alteration was obtained through a report presented by myself and co-authors to the XVIIth International Navigation Congress held at Lisbon in 1949.

Since then, a certain amount of research has been carried out in the Laboratório Nacional de Engenharia Civil, in Lisbon, Portugal, on this subject, and we are now in a position to advance a theory on the causes of this disintegration. Experience shows that *disintegration of portland cement mortar occurs when aggregate is composed of granite in which the feldspar component is altered.* As is well known, sodic and potassic feldspar is altered to kaolin by weathering. When this kaolinized feldspar is an aggregate component of a portland cement mortar maintained in sea water, a reaction takes place between the sea water sulfates and the alumina of the altered feldspar. The result of this reaction is the formation of a sulfoaluminate, and as such reaction takes place in a medium saturated with lime, with a pH higher than 12—as is the medium furnished by the hydration of portland cement—the formation of an expansive sulfoaluminate is obtained. We are then in the presence of a classical phenomenon of portland cement mortar disintegration in sea water. The formation of ettringite is obtained through reaction between sulfate from sea water, alumina from the aggregate, and calcium hydroxide from the hydrated portland cement.

Experience also shows that the replacement of part of the portland cement in the mortar by a good quality pozzolan is a means for counteracting this type of disintegration. In this case, the pozzolan combines with calcium hydroxide, and a decrease in the alkalinity of the medium of hydrated cement is obtained. Then, when sea water sulfate reacts with alumina from the kaolinized feldspar, formation of ettringite does not occur, as this reaction takes place in an unsaturated solution of calcium hydroxide.

When granite with sound feldspar is used as aggregate in a mortar or concrete exposed to sea water no corrosion occurs. Nevertheless, altered granite is used without any inconvenience in general construction works. Actually, in a certain region of northern Portugal, in which the harbor of Leixões is located, this altered granite is used as a mortar and concrete aggregate without difficulty, provided the concrete will not be exposed to sea water.

Figure 1a shows mortar prisms made with a granitic aggregate in which the feldspar component is kaolinized (São Gens granite), after being exposed to sea water for 2 yr and for 6 months. The mortar is completely destroyed after 2 yr; the first signs of corrosion appear at 6 months.

In figure 1b the same is shown except that the aggregate was a granite with its feldspar component perfectly sound (Madalena granite). No corrosion occurs.

In similar prisms, 30 percent of portland cement was replaced by pozzolan. Figures 2a and b show their appearence after 3-yr conservation in sea water. As is seen, no disintegration occurs. In figure 3, expansion curves of these prisms are shown. These diagrams confirm the results shown in the photographs.

The study of the causes of this kind of alteration is still in progress in the Laboratório Nacional de Engenharia Civil. We have not yet done much experimental work on the problem but hope to do that in the next years.

Some notes already have been published on this subject, but unfortunately in Portuguese,[1] so the authors of the excellent paper under discussion have not had access to them.

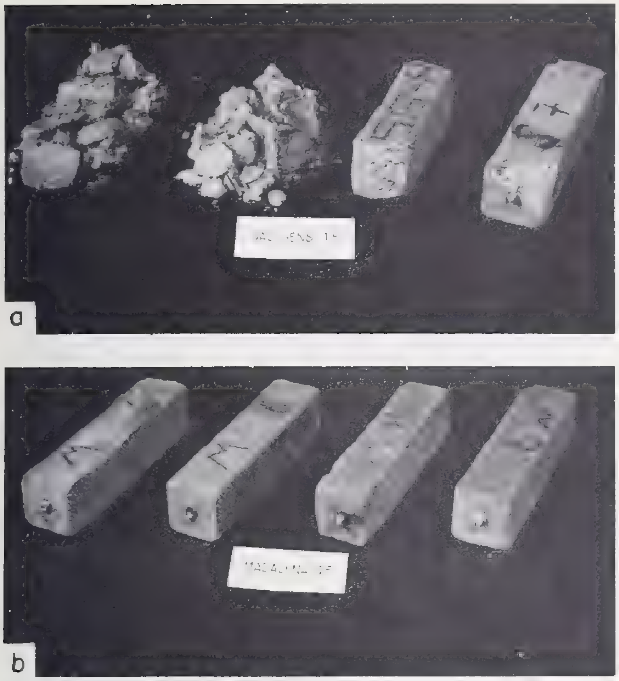

FIGURE 1. *Portland cement mortar prisms of granitic aggregate maintained in sea water.*

Mix proportions: 1 part portland cement to 5 parts of crushed granite between sieves No. 20 and 40.

a. Mortar prisms with kaolinized feldspar (S. Gens), kept for 2 yr (the two at left) and for 6 months (the two at right) in sea water.

b. Mortar prisms with sound granite (Madalena), kept for 3 yr in sea water.

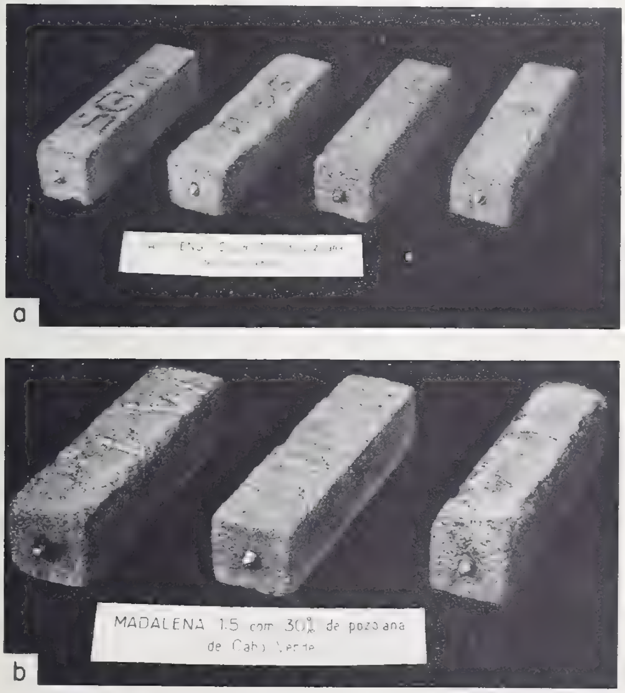

FIGURE 2. *Portland cement and pozzolan mortar prisms of granitic aggregate maintained in sea water.*

Mix proportions: 0.7 parts portland cement, 0.3 parts natural pozzolan of Cabo Verde to 5 parts of crushed granite between sieves No. 20 and 40.

a. Mortar prisms with kaolinized feldspar (S. Gens), kept for 3 yr in sea water.

b. Mortar prisms with sound granite (Madalena), kept for 3 yr in sea water.

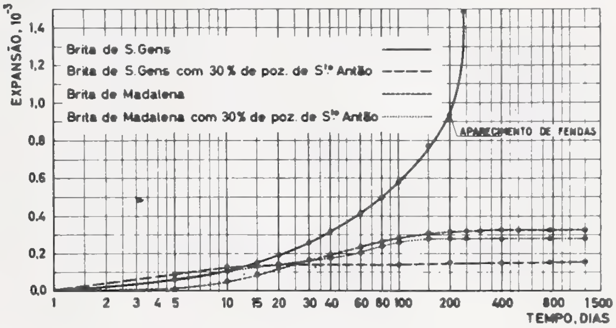

FIGURE 3. *Curves showing the expansion as function of time for the 4 series of prism tests shown in figures 1 and 2.*

(Ordinate: expansion, 10^{-3}. Abscissa: time, days. Legend gives source of aggregate and amount of pozzolan. Arrow indicates appearance of cracks.)

Discussion

Levi S. Brown

Two practical purposes are served in drawing up such a comprehensive and detailed bibliography and review. Though the paper is essentially self-sufficient, some merit may attach to a further word or two in practical application.

Firstly, when faced with a new problem in concrete malperformance, it is human nature to look first to precedent for guidance to explanation. This paper excellently facilitates the search for precedent. Experience however shows that no two cases ever are identical. Every case must be analyzed and judged on its own merits. That is the way precedent is built up.

This approach, while essential, faces two difficulties. The first is imperfect understanding of mechanical features of chemical reactions. One may perceive chemical products that obviously are secondary, yet perceive no proof that their production has been mechanically damaging. The second is that malperformance usually represents the combined effect of many factors. Usually also some one of these factors opened the way to contributory action of the others, but it can be difficult to perceive which one effected initial damage.

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[1] A. de Sousa Coutinho. Pozolanas, betões com pozolanas e cimentos pozolânicos, Técnica, July 1958, No. 283.

A second purpose for a review such as this paper is to forestall recurrence of similar trouble in future construction, that is, to provide a basis for preventive measures. For example, the risk of alkali-aggregate deterioration should be diminished by keeping alkalies and reactive aggregates, insofar as they can be recognized, out of the concrete. There will be cases where neither can be avoided, completely.

But experience has shown that the presence of incompatible components in concrete does not of itself lead to deleterious action. Perhaps no concrete has ever been completely at equilibrium, either within itself or with its surroundings. That is, there are conditional features or circumstances, not in themselves sources of energy, which permit or open the way to deleterious action. Thus they may be called permissive features.

There is nothing new about this concept. It simply means that a quality concrete can be expected to endure and continue to serve its designed purpose. Of course, that is another way of saying that proper attention is given to composition of the cement and reactivity of the aggregate. The more common implications, however, are those of adequate cement factor, low water-cement ratio, perfect mixing, proper placing, protection, and curing. The extended variety of inimical agents reviewed in this paper leads to an impression that good concrete, that is, concrete that long endures in performance of its designed function, is the exception rather than the rule. Actually, with assiduous attention to these so-called quality factors, malperformance itself is the exception.

Discussion

R. Wyatt and G. C. A. Schuit

Silica (opal) when contacted with an alkaline solution will depolymerize according to the equations

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + 2\mathrm{OH}^- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^- + {}^-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}-$$

This causes a swelling essentially due to the incorporation of water and (earth) alkalies penetrating into the concrete structures from the environment. Thermodynamically this is equivalent to an increase in osmotic pressure. The two explanations, the thermodynamic and the mechanistic, are therefore not necessarily in conflict. In fact, they represent two alternative manners of describing the same phenomenon.

Movement of $\mathrm{Ca^{2+}aq}$, $\mathrm{Na^{+}aq}$, and $\mathrm{OH^-}$ ions into an amorphous structure such as silica (opal) will not be determined in the first place by the size of the hydrated ions because their radii are almost equal, due to the presence of hydration water.

The important point is the chromatographic effect that occurs, since the Ca—O—Si bond is far more stable than the Na—O—Si bond. (Ca silicates are relatively insoluble, while Na silicate is soluble.) Hence, if a mixed solution of $\mathrm{Ca^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{OH^-}$ is allowed to penetrate into a silicate column there will occur ion exchange because of the presence of OH groups on the surface of the silica.

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{Ca^{2+}} + 2\mathrm{OH^-} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Ca}\ldots\mathrm{OH} + \mathrm{H_2O}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{Na^+} + \mathrm{OH^-} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Na} + \mathrm{H_2O}$$

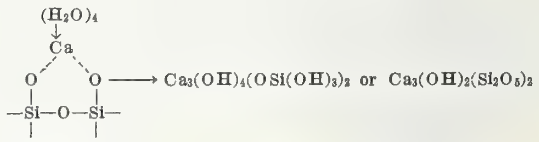
$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Ca}\ldots\mathrm{OH} + \mathrm{Na^+} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Na} + \mathrm{Ca^{2+}} + \mathrm{OH^-}$$

Since the relative residence time of the $\mathrm{Ca^{2+}}$ ions may be assumed to be much longer than of the $\mathrm{Na^+}$ ions, the outer parts of the silica will be enriched in $\mathrm{Ca^{2+}}$ while $\mathrm{Na^+}$ together with its counter ion $\mathrm{OH^-}$ will be able to move further in.

It is our contention that the first product formed by the penetration of $\mathrm{Ca^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{OH^-}$ into the silica is a surface compound of $\mathrm{Ca^{2+}}$ by replacement of surface protons from the OH groups. As has been stated, this occurs preferentially at the outside of the opal particles.

Parallel to this reaction a second one occurs which is essentially akin to the solution of silica in a basic solution, i.e., breaking of Si—O—Si bonds. This reaction occurs as a consequence of the penetration of (earth) alkali and $\mathrm{OH^-}$ ions into the structure.

A slower but possibly important reaction is the conversion of the surface layer of $\mathrm{Ca^{2+}}$ on hydrated silicate, present at the outside of the silica, into a more crystalline Ca hydrosilicate.


$(\mathrm{H_2O})_4$
Ca
O
O
Si
O
Si
$\mathrm{Ca_3(OH)_4(OSi(OH)_3)_2}$ or $\mathrm{Ca_3(OH)_2(Si_2O_5)_2}$

The results of Brunauer et al. strongly suggest that this conversion occurs for Ca compounds, while it has been proven for Mg and Ni silicates by Strese and Hofmann, Feitknecht and Berger, Van Eyk van Voorthuyzen and Franzen (Rec. trav. chim. **70,** 793 (1951)). The reaction readily occurs in some hours at 100 °C. At ambient temperature it is probably much slower but even then may well occur if sufficiently long times of reaction are assumed.

Discussion

G. M. Idorn

Research has aimed at knowledge of the properties of the calcium aluminate sulfates and on their influence on concrete through more than a hundred years. Most of this work has been based on the hypothesis that crystallization accompanied by volume increase of the "cement bacillus" was a major cause of expansion and concurrent disruption of concrete exposed to sulfate solutions, e.g., sea water. Later on, studies of the influence of the calcium aluminate sulfates on the initial setting of portland cement paste also commenced. And most recently, successful efforts both in the USSR and in the United States of America have proved that expansive forces ascribed to the crystallization of calcium aluminate sulfates can be controlled and utilized for prestressing of concrete members instead of external mechanical devices. This development may be said to reflect a remarkable range of opinions on the calcium aluminate sulfates: Once considered a common cause of rapid and severe deterioration, today utilized as a means of manufacturing concrete according to the most advanced constructional principles.

Admittedly a pessimistic view could emphasize that such self-stressed concrete has not yet proved durable, but an optimistic view might rather ask whether also other detrimental agencies upon further research possibly could be tamed and utilized. Today, expectations of a such kind may with some right be stamped as banalities, and one might prefer the more limited question: to what extent still nonrevealed factors are involved in the chemical reactions between aggregate particles and components of cement paste in concrete.

This question comes to the mind of the writer, reconsidering the general report: Chemical Reactions Involving Aggregates, the many interesting contributory papers, and supplementary information collected during recent visits in the United States of America, excellently guided by experienced colleagues.

The contribution by A. de Sousa Coutinho concerning the Port Leixões case, referred to in the general report, ought to receive much attention. The described disintegration of concrete exposed to sea water occurred only when the feldspar in granitic aggregates had been kaolinized (by weathering). Alumina released from the kaolinite was found to react with the sulfates of the sea water and with the calcium hydroxide of the cement paste, forming expansive calcium aluminate sulfates. These findings are of interest in other respects. They bring in mind the early investigation by J. C. Pearson and G. F. Loughlin [1],[1] treating disintegration due to reactivity of altered feldspar but, as far as can be seen now, without the presence of excessive sulfates. Also the severe reactivity of the Norwegian alum shale, referred to in reference [5][2] and of the cinder slags, described in reference [6][2] of the general report, should be considered in this connection. Furthermore, as Mr. Coutinho refers to pozzolanic admixtures as a suitable means of counteracting the described disintegration, attention should also be directed to the investigation by W. Eitel [2]. It is for instance mentioned in this paper that some pozzolans, excellently serving their purpose in concrete in sea water, may create expansive reactions in stronger sulfate solutions, dependent on the alumina present in the pozzolan.

All in all, the above-mentioned studies seem to demonstrate the need of renewed treatments of the lime-alumina-sulfate-water system, aiming at a more accurate description of the potentially expansive combinations of cements, admixtures, and particular rock types in aggregates, and with due regard also to the environmental exposure conditions, the structural qualities of concrete (e.g., permeability), and the constructional principles. The need of low-C_3A cements for concrete in sea water may be considered one subject of such studies, and the further development of self-stressing cements may be another. As a whole it is important to remember that the range of deleterious combinations within the outlined system is only a small part compared with the area of beneficial combinations. However, it should also be borne in mind that with deleterious combinations exceedingly rapid and disastrous deterioration has been experienced in several cases.

The basic description of the alkali-aggregate reactions seems to have been the subject of most discussion, whereas to a regrettable extent the practical aspects have received less attention.

W. C. Hansen claims in his contribution that "the fundamental nature of the alkali-aggregate reactions is understood". Judging from other contributions, however, there seem to remain rather different opinions about this fundamental nature. The writer feels that to some extent the disagreements can be ascribed merely to differences of terminology concerning these rather new fields of colloidal chemical-physical problems. But even with this in mind considerable uncertainty remains.

Little is still known about the relative reactivity of different silica minerals—and this is a question of the chemical nature of the reactions. Neither has the influence of particle size of coarse aggregates been sufficiently studied as a means of disclosing the mechanical nature of the reactions. Furthermore, the necessity of an initial precipitation of a lime-alkali-silica complex in the boundary area of a reacting particle before expansive pressure can develop, is emphasized by some of the authors. But other authors have found that the hardened paste itself can act as a membrane for osmotic pressures, and seem not to agree in the significance of two different types of reaction products.

The possible formation of "reaction rims" in the boundary areas of reacted particles, the composition of such rims, the reasons why and the ways in which they form are problems closely connected with the above-mentioned theories.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] References in Paper VI-1.

It appears from earlier papers (see for instance W. C. Hanna, p. 93, in reference [32][2] in the general report) that a reaction rim may be a rather solid outer shell of a reacted particle in which the interior has been more or less dissolved and weakened.

Such observations tend to support the hypothesis that a nonswelling lime-containing complex is the reaction product in the boundary zone surrounding the less stable alkali-silica complex without lime in the interior. However, a different type of reaction rim appears in figure 1, showing a reacted particle of dense, black flint in cement paste. The boundary zone (white in the photograph) in this case merely represents a depth of penetration inward from the surface of a partial dissolution of the silica structure (chalcedonic) of the flint, whereas no sign of reaction can be detected in the interior of the particle. Hence, the gel that flowed through cracks to the surface of this specimen originated from the boundary zone.

Incidentally, one similiarity between the classical alkali-aggregate reactions with siliceous aggregates and the cement-aggregate reactions may prove to be the formation of reaction rims, as excellently demonstrated by R. E. Bisque and John Lemish [3], and discussed by the latter in his present discussion. In the oral discussions of the symposium the writer mentioned that investigations of concrete deterioration ought to utilize field examinations of concrete structures to a much higher extent than hitherto. If such examinations are undertaken by especially trained inspectors having a background in basic research on deterioration, and if modern recording devices and adequate statistical treatment of data are utilized, information which we are lacking today on actual conditions of concrete deterioration could rapidly be collected and interpreted, in many countries where concrete is a prevailing structural material, to the benefit of the many other countries where concrete is going to be a prevailing means of technical development.

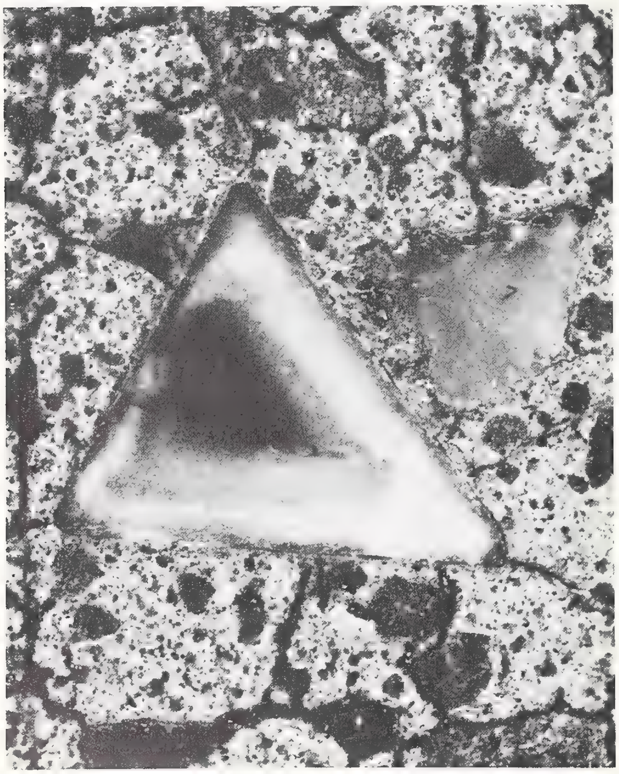

FIGURE 1. *Triangular particle of dense, black flint in cement paste*

Through some months of alkali-aggregate reactions cracks with gel developed on the outer surface of the cement-paste bar. A thin-section revealed the shown partial dissolution of the boundary zone of the flint. The interior of the particle appears to be unaltered.

The shortest edge of the particle is 4.5 mm true length.

L. S. Brown mentions correctly in his contribution that interpretations of field examinations will always have to face difficulties due to:

1. Incomplete understanding of the mechanical effects of chemical reactions, and
2. The complexity of natural detrimental exposure.

It is, however, the experience of the writer that the significance of the mechanical feature of chemical reactions in concrete is frequently more clearly demonstrated in concrete structures than by selected laboratory experiments designed with consideration to available methods of measurements rather than to the structural conditions. (An illustration of this opinion is briefly outlined in the general report, with reference to figure 13.)

It is also the experience of the writer that the complexity of phenomena of deterioration does not always present insurmountable problems. Several cases can be found of concrete failures that are not at all complex and where accordingly a prevailing type of deterioration can be isolated and studied. Such studies of course facilitate the investigations of more complex cases.

Some observations on the mechanism of alkali-aggregate reactions appeared to the writer during a recent visit to the King City Bridge in California. This structure is referred to by Th. E. Stanton on p. 57 in his paper, reference [32][2] in the general report. It was built in 1919–1920 across the Salinas River west of King City, Monterey County. Within 3 yr after construction, cracking was in evidence in the caps of the piers, and later on the cracks extended into the columns of the piers. In 1940 the cracking apparently had been extensive, see, e.g., figure 1e in the above paper. The condition on November 13, 1960, appears from figures 2 and 3. The bridge is still in use leading the heavy traffic of U.S. 101 over the river, and general repair does not seem to have been undertaken. The following observations may claim some interest:

1. The deterioration seems to have progressed only very little or not at all since 1940. Maybe disruption ceased even much earlier. It was not visible whether all available alkalies have been

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[2] Reference in Paper VI–1.

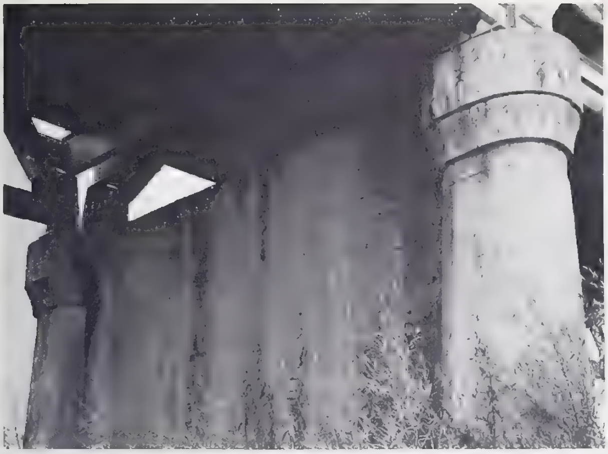

FIGURE 2. *King City Bridge, Monterey County, California.*
Built in 1919 to 1920.
Affected by alkali-aggregate reactions.
Note that deterioration is severe in columns and pier caps, whereas diaphragm wall is undamaged.

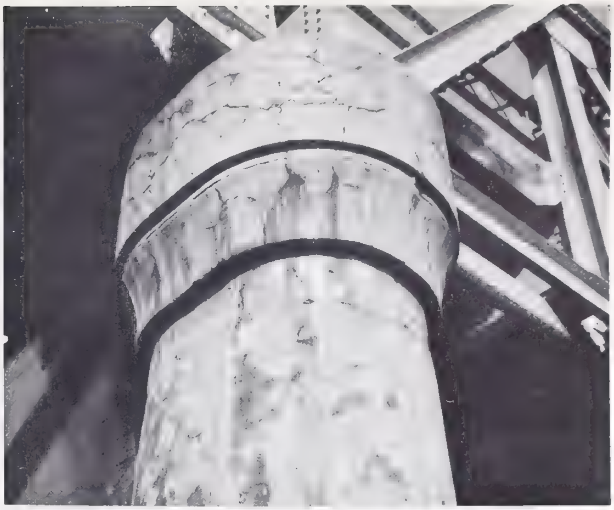

FIGURE 3. *King City Bridge. Pier cap with typical map cracking.*

consumed or all reactive particles have been dissolved, or whether reactions still are continuing, either in a nonexpansive phase, or still expansively, but without further external cracking.

2. Cracking has appeared in the columns and the caps of the piers, but only to a minor extent in the diaphragm walls between the columns. although the concrete composition seems to be the same. This feature is repeatedly met in structural failure caused by alkali-aggregate reactions, i.e., protected parts crack less than exposed areas. The predominant climate conditions are unfortunately not well recorded, and no data are available that could help explain the fact that the north caps and columns are as much affected as are the south ones in this east-west directed bridge.

3. Vertical cracks are seen to prevail downward on the column shafts whereas the caps show extensive pattern-cracking, see figure 3. This feature might be due to differences in either chemical, physical, or mechanical conditions. Laboratory experiments have not always taken all these possibilities into account.

4. Cracking is the prevailing visible evidence of the reactions. Both pop-outs and gel exudations are very infrequent. Could the absence of pop-outs possibly have something to do with the absence of freezing and thawing, and may the lack of gel exudations result from the dryness of the climate, or be related to the season at the date of visit? Obviously these questions need more field examinations as basis for clarification.

5. The climate is apparently very dry, if not arid, but heavy rain had fallen the day before the visit. Is rarely occurring humidity possibly a factor leading to rapid development of the reactions rather than a constantly humid climate or constant aridity? Or may it possibly be that the reactions are only insignificantly influenced by external humidity?

Even more problems could be outlined on the basis of the behavior of the King City Bridge in order to encourage a close correlation between theories and experience in practice. Twenty miles south of King City the San Ardo Bridge, very similar to the above mentioned in construction and size, showed quite the same type and extent of deterioration. Apparently this structure was also a clear-cut case of deleterious alkali-aggregate reactions. But within the next 50 miles at least two similar bridges over the Salinas River are found without evidence of the reactions.

Most authorities consider—as Th. E. Stanton did—the use of respectively high- and low-alkali cements to be the reason for this apparent anomaly. Accordingly, cements with less than 0.6 percent equivalent Na_2O are generally prescribed wherever aggregates known to contain reactive constituents are met, or such aggregates are abandoned.

Repeated field inspections have confirmed that deleterious reactions as a structural problem are effectively counteracted both in these ways and, particularly in dam constructions, by use of pozzolanic admixtures.

More rarely, a choice is at hand between alternate types of aggregates, reactive or definitely nonreactive, or it may be possible sometimes to rely upon improvement of reactive aggregates, e.g., by heavy-medium flotation.

The widespread success in structural practice of these safeguards has established a favorable situation for further research on alkali-aggregate reactions.

The problems have been faced and given attention by comparatively many authorities and individuals. The most urgent demand for solutions has been met by the above mentioned means. The exceptional cases, in which these are going to prove insufficient, will offer excellent possibilities for systematic examination. At the same time, advanced research is to be continued on basic chemico-physical problems of the reactions, as appears from the present series of discussions.

The writer does not consider the now-presented information on the so-called cement-aggregate reactions sufficient to form a general hypothesis on the fundamental nature of this type of deterioration. In fact the presentations by John Lemish and associates, and results reported by H. Hadley at the Portland Cement Association during the Symposium seem to indicate that we ought to consider chemical reactions between components of portland cement paste and of minerals in aggregates in a broader aspect than has usually been done hitherto. The traditional alkali-aggregate reactions might be only one type of mutual reactivity. Other types of such reactivity may be beneficial (and therefore still not recognized). Even the adhesive forces of the contact phase might be studied according to these concepts.

In conclusion, the writer wants to mention certain phenomena referred to by John Lemish in his paper of discussion. Deleterious reactions in dolomitic, argillaceous limestones proved to involve migration of silica ions from the cement paste to the reaction site in the aggregates. If this observation means that silica by internal reactions may be released from the binding constituents of the paste, this would account for a mechanical picture of the deterioration, involving both cracking due to heterogeneous expansion originating from reacting aggregate particles, and crumbling due to partial dissolution and concurrent weakening of the paste. It could possibly also account for loosening of the bonds between aggregates and paste.

Most investigators of structural failures seem to have experienced that by traditional alkali-aggregate reactions the concrete will normally be "sound between the cracks", and figures 2 and 3 of this discussion can be taken as one confirmation of this concept. However, in field concrete (highway pavements) affected by the dolomitic reactivity a general disintegration and weakening both of cement paste and of reacted aggregates have been experienced rather than structural expansion and typical map-cracking.

It seems that proper attention ought to be paid also to this difference by further attempts to enlighten the basic theoretical and practical problems of chemical reactions involving aggregates.

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[2] W. Eitel, Recent investigations of the system lime-alumina-calcium sulfate-water and its importance in building research problems, J. Am. Concrete Inst. **53,** 679–698 (1957).

[3] R. E. Bisque and John Lemish, Silicification of carbonate aggregates in concrete, Highway Research Board, Bull. **239,** 41–55 (1960).

Closure

Niels Munk Plum

It is with the greatest interest that we have studied the five contributions to the discussion which was presented at the symposium, and also the four contributions which have later appeared by correspondence.

The well-prepared contributions have altogether thrown so much light on the present knowledge of the subject that the author is left with the satisfying feeling of a most effective symposium, though it leaves little necessity for concluding remarks.

Mr. Lemish has presented such evidence on the subject of unidentified cement-aggregate reactions that it leaves little doubt as to their character being definitely different from the "common" alkali-silica reactions. As minerals similar to those with which Mr. Lemish has been working may be found in other parts of the world, it is hoped that research on this interesting subject will be continued.

Mr. Hattiangadi stresses the nonexistence of a "safe" limit of the alkali content of the cement. This realization is in our opinion very important and strongly supported by the evidence which we have presented in our paper from our Danish tests.

We are grateful for the contribution from Mr. Hagerman as we had only been able to refer to his work very briefly in the general report.

Concerning the contributions from Messrs. Pike, Hubbard, and Newman, Wyatt and Schuit, and Coutinho we feel that they have thrown new light on a number of important questions on which more research certainly is needed, but we find that at this place an extended discussion will not be of much value.

Mr. Brown has made some very interesting remarks on the scope of research on the performance of concrete with which we are quite in accord. We regret if the general report has given the reader the impression that durable concrete is the exception rather than the rule. Even in Denmark where very heavy deterioriation is taking place, by far the greater part of our concrete is performing very well. The reader must, however, excuse the fact that we are more interested in deteriorating concrete and upon second thought he will certainly also understand why.

Finally a vivid discussion has taken place between W. C. Hansen and T. C. Powers, mainly on explanation of phenomena which have previously been described in the literature. We find that the arguments presented by Mr. Powers are very convincing and strongly supported by his evidence, and if a judgment is needed at the moment, we think that we can quite safely leave it to the reader.

Paper VI-2. Frost Action in Concrete *

Poul Nerenst

Synopsis

Considerable progress in knowledge of the different physical properties of concrete has been achieved within the last ten years. Extensive basic research carried out by T. C. Powers and his co-workers at the Portland Cement Association Laboratories in the U.S.A. has also given a much more detailed picture of the various mechanisms of freezing which pertain to hardened concrete.

Freezing of a porous body may cause damage: (1), by macroscopic ice segregation; (2), by microscopic ice formation combined with a drying of cavities with very small dimensions; or (3), by hydraulic pressure generated by the freezing of water in the capillaries.

Freezing may cause rupture of the paste or of the aggregate. The development of air-entraining agents has made it possible to make cement paste which in the hardened state has very high resistance to freezing and thawing. The beneficial effect of the air bubbles may be explained by the hydraulic-pressure theory and the diffusion theory.

The aggregates used in most countries are dense and of high durability to freezing, but difficulties may arise in some countries where porous aggregates are a main part of the available material for concreting. A short review of the theory and of laboratory experiments to determine the freezing resistance of aggregate is given.

Freezing of concrete during the setting period and in the initial stage of hardening may cause serious damage. This problem is of great economic importance to the northern countries, and a number of tests have been performed recently to determine the required prehardening period to avoid damage from freezing at early ages.

Résumé

Des progrès considérables dans la connaissance des différentes propriétés physiques du béton ont été accomplis au cours des dix dernières années. Des travaux de recherche fondamentale extensifs effectués par T.C. Powers et ses confrères aux Laboratoires de la Portland Cement Association aux Etats-Unis, ont également fourni une représentation beaucoup plus détaillée des différents mécanismes de congélation qui on rapport au béton durci.

La congélation d'un corps poreux peut occasionner des dégâts: (1) par ségrégation macroscopique de la glace, (2) par formation de glace microscopique jointe à un séchage de cavités de très petites dimensions, ou (3) par pression hydraulique produite par la congélation de l'eau dans les capillaires.

Le gel peut causer une rupture de la pâte ou de l'agrégat. Le développement d'agents d'entraînement de l'air a rendu possible la fabrication de pâtes de ciment qui présentent à l'état durci une très haute résistance au gel et au dégel. L'influence bénéficielle des bulles d'air peut être expliquée par la théorie de la pression hydraulique et la théorie de diffusion.

Dans la plupart des pays, les agrégats utilisés sont denses et présentent une forte durabilité au gel, mais dans certains pays des difficultés peuvent paraître où les agrégats poreux forment la plupart des matériaux disponibles pour la fabrication du béton. La théorie et des expériences de laboratoire pour déterminer la résistance de l'agrégat à la congélation sont rapidement passées en revue.

La congélation du béton pendant la période de prise et dans le stade initial de durcissement peut causer de sérieux dégâts. Ce problème est d'une grande importance économique pour les pays nordiques, et un certain nombre d'expériences ont récemment été effectuées afin de déterminer la période de prédurcissement nécessaire pour éviter les dommages dus à la congélation pendant les premiers jours de maturation.

Zusammenfassung

In den letzten zehn Jahren wurde viel Neues betreffs der physikalischen Eigenschaften des Betons gelernt. Die Fundamentaluntersuchungen, die T. C. Powers und seine Mitarbeiter in den Laboratorien der Portland Cement Association in den Vereinigten Staaten unternommen haben, haben sehr dazu beigetragen, daß man sich heute ein besseres Bild von den verschiedenen Gefriermechanismen machen kann, die im erhärteten Beton vorkommen können.

Das Gefrieren eines porösen Körpers kann einen Schaden hervorrufen wegen (1) makroskopischer Eisabscheidung, (2) mikroskopischer Eisbildung, die mit einer Austrocknung von sehr kleindimensionierten Löchern Hand in Hand geht, oder (3) hydraulischen Druckes, der durch das Gefrieren des Wassers in den Kapillaren hervorgerufen wird.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the laboratories of Danish Gas Concrete, Inc., Virum, Denmark.

Das Gefrieren kann eine Zerstörung der Masse oder der Zuschlagstoffe hervorrufen. Die Entwicklung der luftzuführenden Mittel hat es möglich gemacht, eine Zementpaste zu erzeugen, die im erhärteten Zustande gegen Einfrieren und Auftauen sehr widerstandfähig ist. Der günstige Einfluß der Luftblasen kann an Hand der Theorie des hydraulischen Druckes und auch mit Hilfe der Diffusionstheorie erklärt werden.

Die Zuschlagstoffe, die in den meisten Ländern verwendet werden, sind dicht und sehr beständig gegen ein Einfrieren, aber in einigen Ländern, in denen überwiegend poröse Zuschlagstoffe für Beton angewandt werden, muß man Schwierigkeiten erwarten. Eine kurze Übersicht über die Theorie und die Laboratoriumserfahrungen der Bestimmung der Einfrierwiderstände der Zuschlagstoffe wird gegeben.

Das Einfrieren des Betons während der Erstarrung und in der ersten Erhärtungsstufe kann einen großen Schaden hervorrufen. Dieses Problem ist wirtschaftlich für die Nördlichen Länder sehr wichtig und eine Reihe von Untersuchungen ist kürzlich angestellt worden, um die nötige Vorhärtungszeit zu bestimmen, sodaß man einer Beschädigung durch ein Einfrieren frisches Betons vorbeugen kann.

Introduction

Deterioration of concrete due to freezing action has been observed in a great number of structures exposed to water and low temperature. The damage caused by freezing has possibly involved higher expenditure to repair than any other destructive force.

Before the second World War an exact knowledge of the factors influencing the resistance of concrete to freezing and thawing were not well known. It was the general idea, however, that strong concrete also would be durable. In the older days when the cost of labor was comparatively lower, and the speed of construction was not as important as today, a number of structures were built with sufficient strength and high durability.

At the 100th anniversary of the use of portland cement in Denmark in 1960, a photograph was shown of a fortress built in the sea east of Copenhagen (fig. 1). The work was begun in 1860 and continued during various periods before 1880. The concrete is today in excellent condition in spite of the exposure to water and freezing-and-thawing cycles.

The ideas of making good concrete are much older than 1918, when Abrams formulated the relation between water-cement ratio and strength. H. L. Childe [1],[1] the managing editor of "Concrete and Constructional Engineering," is to be credited for having quoted a prescription for making good concrete, which was found in a book on concrete written by Henry Reid, a civil engineer, and published in 1868.

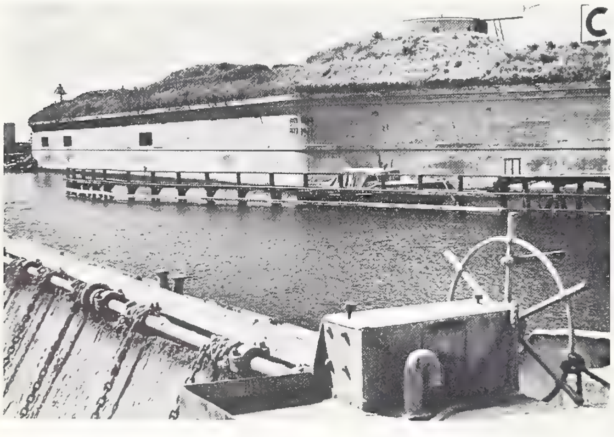

FIGURE 1. *Concrete structure near Copenhagen of an age of 100 yr.*

(G. M. Idorn)

"The due and thorough incorporation of the cement, sand, shingle or gravel, with the least amount of water, is the ABC of the process of concrete making, and unless this is rigorously attended to much disappointment will be experienced. The whole of the ingredients should be well mixed first in a dry state, and when this is thoroughly done a quantity of water added to render the mixture plastic enough to be put into moulds or placed between the boards used for forming the walls. As a rule the less quantity of water you can use the better. The concrete should be well rammed in as dry a state as is consistent with the proper requirements of the material, for too small a quantity of water would be quite as injurious as an excess; again, that would be materially influenced by the amount of percussion applied by the impingement of the rammer. The rammer should be as heavy as can conveniently be used. Sand, where a choice exists, should be as rough and coarse as possible. A rotten or friable aggregate is to be avoided. The sand must fill up the vacuities in the compound. Where practicable, concrete blocks should be placed for some days or weeks in water. Concrete, when so treated and carefully and thoroughly mixed, will be immensely superior in quality to the ordinary sloppy and roughly-handled mixture commonly called concrete, only in many cases entitled to the name because it contains certain proportions of the necessary ingredients."

In the twenties and the thirties of our century the wet concrete mixes were growing in popularity, foremost in the United States, but also in many countries in Europe, and the freezing resistance of concrete was diminishing. The low durability of concrete roads was growing to be a serious problem, and was presumably one of the reasons for launching the big research program, "Long-time Study of Cement Performance in Concrete," in 1940 [2]. A few years earlier the beneficial effect upon the freezing resistance resulting from entrained air was discovered in the U.S.A., and much work has since been devoted to research on air-entrained concrete and its properties and manufacture.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The use of air-entrained concrete was only slowly and reluctantly adopted in Europe within the last decade, but even today you may in many quarters in Europe find die-hards, who as yet are not convinced that air-entrainment is an advance of the utmost importance for concrete durability, mostly because they do not want to sacrifice a few percent of the strength in order to get a much higher durability.

The professional and unbiased engineer is ready to adopt a new material or method if all empirical data tell him that good results can be obtained, without knowing the basic and chemical laws involved in obtaining the good results. Portland cement has, for example, been used for several hundred years, although the nature of the hydration products has been the object of vigorous discussions at all symposiums on cement chemistry so far, and it is not to be expected that a final agreement will be reached at this symposium either. The use of air entrainment was adopted in the United States 20 years ago, but a qualitative explanation of the mechanism of freezing air-entrained concrete has been developed within the last decade. Taking into consideration the very complex nature of freezing phenomena, the progress is very notable, and it is mainly due to T.C. Powers and his co-workers at the Portland Cement Association.

The number of reports and studies published on freezing action is so large that it is almost impossible to cover all the aspects of the subject in the present paper in a balanced form. Some excellent reviews by Powers [3] and Möller [4] have been very valuable in the preparation of the present paper, which consequently does not pretend to contain many new points of view.

The first part of the paper deals with the freezing of hardened concrete, where most of the physical properties of the ingredients have definite levels. The different mechanisms of freezing and the effects upon the paste and aggregate are summarized. Only a few references to laboratory tests on concrete are given, because a vast amount of test data is difficult to interpret in the light of the basic knowledge of today, as most of the factors governing frost resistance have not been recorded.

A brief summary of test methods employed in measuring the damage caused by frost action is given.

The last part of the paper deals with freezing of concrete at early ages, which is a much more complicated case than freezing of mature concrete, because almost all of the physical properties of concrete are changing as the hydration is progressing.

Some observations on freezing of aggregate and concrete are related from job sites, and a summary is given of tests carried out to determine the required prehardening time to avoid frost damage.

Freezing of Water in Hardened Concrete

The freezing of water in concrete can give rise to stresses and possibly cause rupture either of the paste or of the aggregates. The disruptive forces are due to the well-known fact that conversion of water into ice is accompanied by an increase of volume of about 9 percent.

The freezing point is 0 °C only for pure water in the normal-stress condition. The water in concrete often contains small amounts of alkalies, which cause a depression of the freezing point, preferably called the melting point to avoid the influence of supercooling.

The melting point of ice is also dependent upon the size of the cavities or pores where the water is situated, as pointed out by Powers and Brownyard in 1947 [5]. For most aggregates having noticeable porosity the size of the pore structure is such that the depression of the melting point is insignificant.

The hardened paste is characterized by a very high porosity combined with pores and interstitial spaces of exceedingly small dimensions. The result is that only part of the water freezes at temperatures just below 0 °C. When the temperature is lowered, increasing amounts of water are converted into ice, but even at —78 °C some of the water in the most narrow spaces within the gel is unfrozen.

In the following considerations it is assumed that the paste has an internal structure (fig. 2) as described by Powers and Helmuth in 1953 [6]. Later observations by Åke Grudemo with the electron microscope have shown that the hydration product consists of slender ribbons and crumpled sheets, so that the idea of the sphericity of the gel particles cannot be maintained. This has,

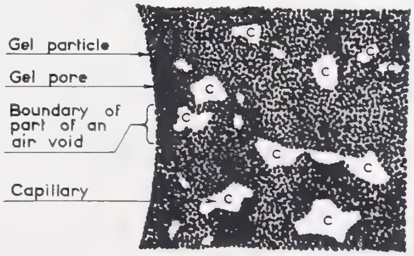

Figure 2. *Model of capillaries and gel in hardened portland cement paste.*

(Powers and Helmuth [6])

however, but little influence upon the conception of the way in which water is fixed in the paste. The water molecules are exposed to forces which depend on the distance from the gel particles.

The greater the distance between the gel particals and the water molecules, the more freely is the water moving in the paste and the higher is the resemblance to water in normal-stress condition with regard to water evaporation, melting point, etc.

After presentation of the general ideas pertaining to the mechanisms of freezing, the paste and the aggregate will be treated separately on account of the big difference between the internal structures of the two components.

Theories of the Mechanism of Freezing

Macroscopic Ice Segregation

Taber [7, 8] has explained how frost upheavals occur in soils, due to macroscopic ice segregation. When free water turns into ice in the larger voids and cavities, the capillary water is drawn from the unfrozen soil, and ice lenses are developed. If the possibility of continued capillary suction of water from the ground-water zone exists, the ice lenses will grow, and the result will be frost upheavals (fig. 3). The development of the ice lenses is dependent upon the flow of water through the soil and consequently depends upon the capillary suction and the permeability.

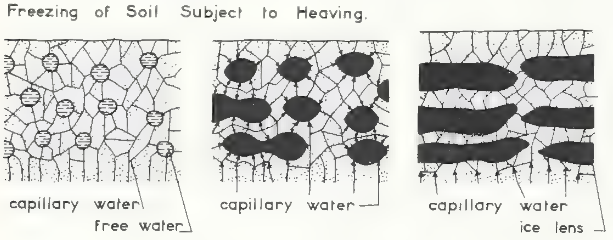

Figure 3. *Mechanism of macroscopic ice segregation in soil.* (Nerenst, Rastrup and Idorn [10])

According to A. Casagrande [9] ice lenses and frost upheaval can be expected in soil of varying grain sizes, if the content of particles below 0.02 mm is higher than 3 percent. In soil of rather uniform grain sizes the content of fine particles may reach 10 percent as shown by the dashed line (fig. 4).

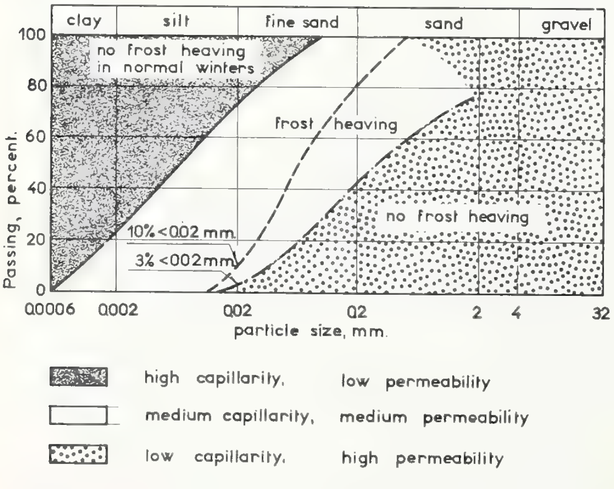

Figure 4. *Interrelation between the possibility of frost upheavals and grading of soils.* (Kögler and Schneidig [9])

Soils with grading curves to the left of the white area will have very high capillarity, but the permeability is so low that no frost heaving will occur in normal winters, as the transport of water from the ground water table is not sufficient to keep the ice lenses growing.

Soils with grading curves to the right of the white area have very high permeability, but the capillarity is too low, so that the water will freeze in place without forming ice lenses.

As pointed out by Nerenst, Rastrup, and Idorn [10] fresh concrete may be considered as an artificial soil, which contains such an amount of fine particles—clay, filler, and unhydrated cement—that the mixture under special conditions is susceptible to the formation of ice lenses according to Casagrande's criterion.

The formation of ice lenses has been used by Collins [11], in Great Britain, as the explanation of the deterioration of low-quality concrete with access to moisture from the surroundings, for instance concrete roads on clay subgrade.

Collins has shown by experiments that cylinders of low-quality concrete frozen from the upper surface show the formation of ice lenses, when the bottom face is in contact with water.

In 1945 Powers [12] presented his paper "A Working Hypothesis for Further Studies of Frost Resistance of Concrete," in which the hydraulic-pressure theory was outlined. Powers stated that the Taber-Collins theory cannot be applied to hardened concrete of average quality, because the growing of the ice lens would be prohibited by the tensile strength of concrete being much higher than the cohesion in soil. He quotes Taber [8], who found that loading of soil often caused it to freeze as a closed system, i.e., a system from which water could not escape and into which water could not enter. Thus Powers at that time thought that ice lenses would not be formed in hardened concrete on a macroscopic scale as in soils, but "it would be reasonable, however, to assume that ice segregation takes place in concrete on a submicroscopic scale. As already pointed out, the hardened paste is considered to be composed largely of a porous gel containing a system of capillaries. If the ice forms only in the capillaries, as seems likely, then we may imagine it to be forming in a container having porous, water-laden walls of gel. Hence, the ice could and probably would receive water from the walls as well as from the more open capillaries. The amount of water available from the gel is very limited; nevertheless some expansive force due to this effect is probable."

It is interesting to note that although Powers at that time emphasized the hydraulic-pressure theory, he still considered it worthwhile to investigate other mechanisms of concrete deterioration due to freezing. Research work was started at the Portland Cement Association Laboratories in the U.S.A., and the result has been the diffusion theory or the theory of microscopic ice segregation, which will be treated in more detail below.

At the RILEM Symposium in Copenhagen, 1956, Powers [13] drew the conclusion that in mature concrete, macroscopic ice segregation will only take place when the water-cement ratio is above 0.9 by weight and under special climatic conditions, while it is likely to take place in any concrete during the early stages of hydration.

Hence, the formation of ice lenses on a macroscopic scale is further treated in a following section, where freezing of fresh and green concrete is discussed.

Microscopic Ice Segregation

The theory of segregation of ice on a microscopic scale within the cavities of the hardened paste has been presented by Powers and Helmuth [6]. G. Pickett [14] has further given a mathematical treatment of the transport of water in cement paste during freezing.

During the research work carried out in the P.C.A. Laboratories in order to verify the hydraulic-pressure theory it was found that it could be experimentally confirmed, but at the same time it was learned that the hydraulic-pressure theory did not account for all the phenomena observed.

Part of the effect of freezing is apparently due to a tendency of microscopic bodies of ice to grow in locations where the water is little influenced by adsorptive forces, i.e., in the capillaries and voids. The ice bodies draw water from the gel by a diffusion process.

Volume change due to freezing was studied on specimens of neat cement paste in the saturated state, some made with and some without entrained air. The length change was recorded in microinches per minute. The temperature was measured with an accuracy of about 0.1 °C. Several hundreds of experiments were made, in which length change, temperature change, and elapsed time were recorded automatically. Typical results of the tests are shown in figure 5.

It is characteristic that cement paste without entrained air dilates as could be expected; and, accepting the hydraulic-pressure theory, it is also understandable that the air bubbles can relieve the stresses from the hydraulic pressure building up in the pores during the freezing, so that the specimens will contract thermally when the temperature is lowered.

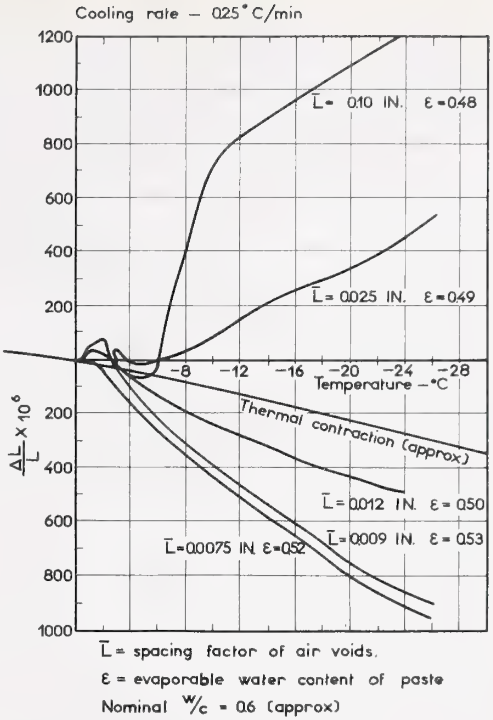

FIGURE 5. *Volume change during cooling of hardened cement paste as influenced by the bubble spacing factor* $\bar{L}$.
(Powers and Helmuth [61])

By closer study it was found, however, that the decrease in length was greater than could be expected from the thermal contraction.

From thermodynamic studies it was concluded that water in the capillaries or on the walls of the air bubbles was forming ice bodies on a microscopic scale, which were able to draw water from the gel by a mechanism similar to that mentioned for macroscopic ice segregation in soils and fresh concrete.

Paste containing sufficient amounts of well-distributed air bubbles will permit this formation of ice without dilating, and as water is drawn from the gel, the overall effect is shrinkage of the specimen, which earlier also was reported by Valore [15].

As the amount of segregating ice depends upon a rather slow diffusion process, the length of the freezing period has an important influence upon the observed changes in length. This is in contrast to the hydraulic pressure, where the rate of cooling is the most important variable of the freezing condition.

The microscopic ice segregation has been further discussed by Powers [13], and it is claimed that this phenomenon will especially apply to mature paste in concrete with rather high cement content, i.e., water-cement ratio below 0.55.

The lower limit of water-cement ratios where this theory is applicable is not determined as yet by experiments. Woods [16] has suggested, that concrete of water-cement ratios below 0.40 would be frost-resistant without air-entrainment. Powers [5] has earlier suggested formulas, from which the amount of freezable water at different temperatures may be computed from the initial water content. From these it was computed that a paste of a water-cement ratio=0.30 would not contain any freezable water at −30 °C after a certain stage of hydration was obtained.

Chapelle [17] has made experiments from which he concluded that the water-cement ratio is the determining factor of freezing resistance, and claims that concrete with a water-cement ratio below 0.45 is damaged only by mechanical stresses due to the alternating temperature. Chapelle does not accept air entrainment as a decisive factor in frost resistance, but emphasizes the influence of the chemical composition of the cement. He states that the presence of pockets of crystals of hydrated lime in the paste without entrained air causes low resistance to freezing.

Hydraulic Pressure

The hydraulic-pressure theory has been developed from concepts earlier used for building materials other than concrete. For clay bricks, it is quite common to correlate the frost resistance with the degree of saturation determined in a standardized way. As water expands about 9 percent when converted into ice, it has been expected that no damage should be caused by freezing a body in which the degree of saturation is below 0.917. This belief is only correct under the assumptions that the water is homogeneously distributed throughout the material and that the water movement caused by the formation of ice does not give rise to stresses.

Whiteside and Sweet [18] applied this concept to concrete, in which the air voids were included when the degree of saturation of the binding matrix—i.e., paste and air voids—was computed. They found, however, that some specimens with a degree of saturation lower than 0.917 deteriorated. Thomas [19] found in 1938 that specimens of rocks at the same degree of saturation dilated differently when the freezing rate changed.

Powers [12] stated that the concept of a critical degree of saturation is not sufficient to explain the behavior of concrete during freezing. This is due to the specific physical properties of the hardened cement paste, which has very high porosity but at the same time a very low permeability. Mature paste with water-cement ratio=0.70 may have a porosity of 50 percent and a permeability of the same order as granite which may have a porosity less than 1 percent [3, 20]. Hence the freezing of nearly saturated paste is accompanied by displacement of water, giving rise to a hydraulic pressure gradient.

On this basis the concept of the critical half-thickness, D_{crit}, is developed.

For thin slabs of paste, D_{crit} is equal to the maximum half-thickness of the body permitting the water to escape through the surfaces without causing damage. Surfaces from which the water may be expelled are termed "escape boundaries."

For air-entrained paste, D_{crit} is equal to the maximum half-distance between the air voids. The walls of the air voids represent a large increase of the escape boundaries.

Assuming that Darcy's law is valid for the flow of water in the hardened paste and expressing that the hydraulic pressure should not exceed the bursting strength of the layer, the following formula is obtained in the notation used by Jessing [21]

$$f(D_{\mathrm{crit}})=\frac{KB}{\left(1.09-\frac{1}{s}\right)w_f\frac{dm}{dt}}, \qquad (1)$$

where $f(D_{\mathrm{crit}})$ (cm^2) may have forms according to the geometrical shape of the paste body or the particle.

K=permeability of material (cm/sec).

B=bursting strength of material (cm head of water).

s=degree of saturation, i.e., amount of freezable water w_f divided by the capacity for freezable water, p.

$w_f\frac{dm}{dt}$=rate of ice formation (cm^3/cm^3 sec).

m=that fraction of water (w_f) which freezes at a given temperature.

It will be seen from eq (1) that the determining factors are the permeability, the strength of the material, the degree of saturation, and the rate of ice formation, which depends upon the rate of cooling.

Hydraulic Pressure in Paste

Structural members of concrete usually are much too thick in comparison with the critical thickness when the paste is saturated and the water-cement ratio has a normal value.

Klieger [22] has found by a comprehensive investigation that non-air-entrained concrete will show great expansion in freezing-and-thawing tests even at water-cement ratios as low as 0.37 by weight. The cooling rate was 11 °C per hour, which is much higher than usually met in the field. During placing of concrete without air-entraining agents air is entrapped in ordinary concrete in irregular cavities and may give some protection at moderate freezing rates, but the amount of air and the distribution of voids is normally not able to give sufficient escape boundaries during the normal freezing procedure employed in the laboratories.

By the use of a suitable air-entraining agent cement paste can obtain a very large number of air voids, which reduces the critical thickness of the layer of paste as each wall of the air bubble may serve as escape boundary. In this way cement paste can attain a resistance to freezing-

and-thawing cycles making it almost immune to frost attack.

In earlier papers it has been stated that the spacing between air bubbles should be of the order of 0.01 in. ($\sim 250\ \mu$) [23] but lately during a discussion of a RILEM Seminar, 1958, Powers [24] stated that the average distance between air bubbles should be kept as low as 50 μ.

Danielsson [25] has refined the mathematical derivation of the hydraulic-pressure theory and suggested the concept of the frost-protected volume, which in his experiments has given a better correlation with the durability factor than the characteristics of the distribution of air bubbles suggested by Powers.

Hydraulic Pressure in Aggregate

The same concept as outlined in eq (1) pertains to the freezing of rock, i.e., the critical size depends upon the permeability, the strength, the degree of saturation, and the rate of ice formation.

In comparison with mature cement paste, the porosity of aggregate normally used in concrete is usually low, as the apparent specific gravity is only a little lower than the true specific gravity. An exception is the cherts, for instance, used in Denmark and in the southeast of the United States of America, in which the porosity may be as high as 10 percent. Similar porosities may be found for special types of limestone.

The pore system in rocks has usually much larger dimensions than in hardened paste. Hence most of the water freezes at a temperature near the melting point of ice. On the other hand the amount of freezable water in the aggregate is much lower than in paste of average quality.

As the pore system in most rocks is formed of capillaries with large diameters, the resistance to water flow is rather low, in comparison to cement paste, when the porosity is taken into consideration as shown in table 1, which was given by Powers in 1956 [20]. Finally, the strength of rocks is high.

TABLE 1. *Comparison of permeabilities of rocks and mature pastes (Powers [20])*

Kind of rock	Permeability of rock, $K \times 10^{12}$	Water/cement ratio of mature paste for same K
	cm/sec	
Dense trap	0. 345	0. 38
Quartz diorite	1. 15	. 42
Marble	3. 34	. 48
Marble	80. 5	. 66
Granite	748	. 70
Sandstone	1, 720	. 71
Granite	2, 180	. 71

From these considerations it follows that most aggregate, when frozen before use in a concrete mix, has a very large critical size in comparison with cement paste. When the aggregate is embedded in concrete the situation is quite different.

Scholer [26], in 1930, had already pointed out that some aggregate is susceptible to frost damage when embedded in concrete even if good results are obtained by freezing tests on the aggregate alone.

Powers [3] explains that the paste is acting as an almost impermeable membrane causing the rock particle to be frozen as a closed container. When the degree of saturation is above a critical limit, which due to mineralogical heterogeneity may be lower than the theoretical value of 0.917, the particle must dilate and give rise to stresses in the surrounding paste.

Determination of Frost Damage

In the following sections test results from experiments with freezing and thawing will be mentioned. In order to give a background for these references a brief survey is given of the methods employed to determine the change in concrete properties as caused by the frost damage.

The discussion is mainly limited to laboratory methods. The first group comprises measurement of the reduction of strength, e.g., compressive and tensile and modulus of rupture. Another group of methods comprises determinations of variations in length or volume of the specimen. The third group comprises determinations of the elastic properties of the concrete by different types of equipment.

Strength Determinations

It is generally accepted that deterioration of concrete caused by a number of freezing-and-thawing cycles is due to the formation of cracks in the hardened cement paste, often combined with reduction of the bond between paste and aggregate. In cases where unsound types of rocks have been used as an aggregate, the stone particles proper may be cracked and deteriorated. Consequently, the reduction of the quality may be revealed in the best way by methods which are sensitive to cracks in the concrete.

The compressive strength is not very sensitive to frost damage, as a large number of minute cracks do not influence the resistance to compression. This situation may be elucidated by considering a concrete cube which has obtained several planes of rupture perpendicular to the direction of load. If we assume rough, interlocking surfaces of the planes of rupture, the cube will have considerable compressive strength almost equal to that of an undamaged specimen, while the tensile strength will be zero. This will be the case even when the planes of rupture are inclined up to a certain angle depending upon the material. Consequently, testing of damaged concrete preferably should be executed in such a way that the tensile strength is a governing factor for the rupture.

While a direct determination of the tensile strength of concrete is not easy to carry out, it is feasible to determine the modulus of rupture. A third-point loading should be preferred, where feasible, as from a statistical point of view it is an advantage that the moment is constant for a great part of the beam length. With loading of the beam in the middle of the span the moment is variable, and rupture will take place where a maximum combination of stress and low resistance exists, which is not necessarily in the middle of the beam.

Variations in Volume and Weight

During the freezing of cement paste or concrete the material is changing in volume not alone during a single cycle of freezing and thawing, but it is also observed that any damage to the concrete will be revealed by residual deformations, whereby the volume of the concrete is increased.

Comparator Measurements

Consequently the progress of deterioration may be followed by measuring the length of concrete specimens at definite intervals by a comparator method, but the length change in itself does not give an estimate of the degree of deterioration. As far as known no definite criteria have been worked out to relate length change with degree of damage, although many laboratories have accepted that a specimen showing an expansion of 0.1 percent represents failure of the concrete. In other laboratories freezing cycles are continued until an expansion of 0.3 to 0.6 percent is obtained [27]. Verbeck and Klieger [28] have recently described an apparatus which automatically records change in length and heat flow, from which the correlation between amount of ice and length may be determined.

Dilatometer Method

The variation in volume of small concrete specimens may be studied by the use of a dilatometer. This method has been used for instance by Powers and Helmuth [6], Valore [15], and Valenta [29], but only specimens of limited size can be used, and the method is consequently more applicable for study of mortar than for laboratory investigations of various concrete mixes.

In connection with the dilatometer method it is important to notice that the measured dilation pertains to the system water–mortar and any growth of an ice layer on the outside of the specimen will be recorded as a dilation of the specimen.

Change of Weight

In earlier studies of the deterioration of concrete specimens exposed to freezing-and-thawing cycles, it has been quite common to estimate damage by determining the change of weight. The results are, however, influenced by disturbing factors. For instance, partly dried specimens will, during the freezing-and-thawing cycles, absorb water and actually increase in weight and may at the same time lose in weight due to spalling. It has also been experienced that concrete specimens have been seriously damaged by freezing and thawing, as measured by the reduction of the dynamic modulus of elasticity, without any weight loss at all. Hence it is concluded that this method should not be used alone.

Elastic Properties

In the last 20 years different apparatus and methods have been developed in the U. S. and Europe to determine the elastic properties of concrete by nondestructive methods, and it is known that the dynamic modulus of elasticity is a rather sensitive and accurate measure of the progressive deterioration of concrete subjected to freezing and thawing cycles.

Resonant-Frequency Method

This method was originally developed in the United States of America and has within the last twenty years been widely accepted. Since 1955 it has been a method of test of the American Society for Testing Materials. From the results obtained it is possible to compute a factor of durability by expressing the measured dynamic modulus of elasticity relative to the initial modulus after a certain number of freezing and thawing cycles.

Wave-Velocity Method

Methods and apparatus for measuring the wave velocity through concrete specimens have been developed in Canada and described by Leslie and Chessman [30]. In Great Britain, Jones has used an apparatus constructed according to similar principles [31] to study the effects of freezing-and-thawing cycles on concrete cubes. In Denmark a condenser chronograph has been developed [32, 33]. Various methods have been developed in France to study the elastic properties of concrete by nondestructive methods [34].

A survey of later developments within this field has been given by Whitehurst and Parker [35], and the merits and drawbacks of the different methods have been discussed by Verbeck [27]. The result of an inquiry to RILEM members has been reported by Jones [36].

It seems that although the resonant-frequency method correlates fairly well with the expansion, some difficulties are encountered in cases where spalling takes place, because the corrections for shape and weight are cumbersome.

The wave-velocity method is not very sensitive to frost damage but may be a suitable indicative method for use in the field.

Visual Observation

This method is among the oldest, and much valuable qualitative information may be gained from observations made with the naked eye by inspections in the field and investigations in the laboratory.

In order to get quantitative measurements, which can be carried out by less-trained personnel, various arbitrary systems of ratings have been chosen, which may serve the purpose by comparisons of different test series. Especially in field inspections, where many different causes of deterioration may be met, the interpretation of observations should be made with great care, and the method calls for an intelligent concrete technologist with broad experience.

The use of petrographic methods in evaluating frost damage is a very promising field for freezing at early ages and for study of aggregate which has expanded and cracked during freezing.

Freezing of Hardened Concrete

In the course of time a tremendous amount of research work has been invested in exposing concrete specimens of varying composition, age, degree of saturation, etc., to artificial freezing-and-thawing conditions with a similar great number of characteristic variables.

It has been common to report the resistance to freezing and thawing of hardened concrete as influenced by cement type, fineness, chemical composition, water-cement ratio, total water content, consistency, grading and amount of sand and stone, maximum particle size, compacting method, curing methods, addition of inert fillers and fly-ash, accelerators, etc.

On the background of the knowledge of today it is to be regretted that all these test data have been the basis for establishing a great number of false correlations or, at best, conclusions which are based upon the appearance of relations between the factors, which only in an indirect and superficial way characterize how the resistance of concrete is affected.

As the test results in most cases are lacking information on the properties of the cement paste, which at present are thought to be of decisive nature, such as air content, void spacing, etc., even for the entrapped air, it is impossible to interpret the older data in the light of the new concepts.

To illustrate this statement reference is made to "Long-Time Study of Cement Performance," chapter 9, where Jackson [37] concludes that the observations from the many field and laboratory studies clearly demonstrate that the chemical composition of portland cement as such has no significant influence upon the resistance to freezing and thawing. This question has been the subject of controversy in America and is still discussed vividly in Europe [17, 38, 39].

The freezing tests in the laboratory have the purpose of obtaining a quick estimate of how concrete would perform when used in actual field structure. In order to obtain the results quickly, the cooling rate has been increased far beyond what can be expected under natural conditions, which may give a distorted picture. The required amounts of air to obtain protection against freezing may by laboratory experiments reach too high values, and some sort of adjustment to actual climatic conditions is recommended. The lacking correlation between laboratory tests and field exposure has, for instance, been studied by Kennedy and Mather [40] and discussed in detail by Powers [3], who suggested a modified procedure of freezing tests, measuring the dilation during cooling at a moderate rate (5 °F (3½ °C) per hour) followed by a period of constant low temperature at −19 °C (0 °F).

The test is carried out between intervals of soaking, each of two weeks duration. When the length of the period of immunity to soaking and freezing has been determined, the specimens may be subjected to successive freezing cycles combined with measurements of the increase of permanent dilation. The suggested procedure should be less expensive than the procedures used at present.

Studies of the methods adopted by the A.S.T.M. in the United States have been carried out by Flack [41] and Arni, Foster, and Clevenger [42]. The characteristics of the freezing procedures used by a number of European laboratories have been reported by Jarrige [43].

Tests on the Freezing Resistance of Aggregate

As it now is possible to produce an air-entrained cement paste which in the mature state is immune to frost action, at least under most natural exposures, more interest is to be placed in the future upon the frost resistance of aggregate, which cannot be improved, if required, in the same easy and economical way as the paste.

The influence of the degree of saturation of chert aggregate upon the freezing resistance of concrete has been studied by Stanton Walker [44], and some of his results are reproduced in figure 6.

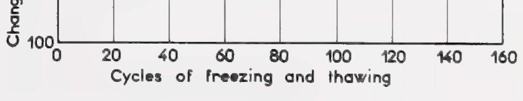

FIGURE 6. *Resistance to freezing cycles as influenced by the degree of saturation of a porous coarse aggregate.*
(Walker [44])

The material with the indication $s=1.0$ (100 percent saturated) was stream wet, and the poor durability obtained shows that porous gravel dug out from rivers or the sea may have initial high water content compared to the same stone material from gravel pits above the ground-water table, as it is difficult to saturate porous material after a drying period.

The frost resistance of stone is especially influenced by the microporosity, i.e., pores of sizes below 5μ. The pore distribution may be determined by measurement of the capillary suction forces by direct suction or by the quantities of water held back during centrifuging.

The sizes of the most narrow capillaries may be determined by measuring the interrelation between the water content and the relative humidity [45].

From these determinations a histogram of the computed pore-size distribution can be prepared, which may be correlated with the resistance to freezing.

Blaine, Hunt, and Tomes [46] have measured the internal surface of stone, bricks, and concrete by low-temperature nitrogen sorption by the Brunauer-Emmett-Teller method [47, 48] and found that stones with high internal surface area have low resistance to freezing. An example of their findings is given in table 2.

TABLE 2. *Surface areas and service records of crushed limestone used in highway concretes [46]*

Limestone No.	Surface area	Reported service records [a]
	m^2/g	
1	0.30	Excellent service record.
2	.78	Good service record.
3	.78	Good service record.
4	1.18	Bad service record, quarry condemned.
5	2.26	Bad service record, quarry condemned.
6	3.63	Bad service record, unsatisfactory perfomrance.

[a] Samples and information on service records supplied by J. E. Gray, National Crushed Stone Assoc.

Measurements on hardened cement paste showed that intentionally entrained air did not cause any significant difference in the measured internal surface area. This result indicates that even if the method is valuable in measuring the microporosity it does not reveal the presence of protective air voids, which also may be found in certain types of dolomite and basalt.

The methods outlined above give more information on the properties of rocks than do determinations of total porosity, which includes both the dangerous microporosity and the beneficial macroporosity.

Wuerpel and Rexford [49] have proposed a flotation procedure using heavy liquids for separation of unsound chert particles. For the materials investigated the unsound materials were particles with a bulk specific gravity below 2.40 after saturation by 5 hours boiling. This limit was based upon field inspection and measurements on particles which had caused "pop-outs."

In Canada and the United States a number of gravel producers have within the last ten years installed equipment for float-sink separation on an industrial scale. The process is called Heavy-Medium Separation, or abbreviated, the H-M-S procedure. Price [50] has made a survey of the H-M-S and other procedures currently used in gravel beneficiation and has reported results which indicate a significant improvement of the treated materials with regard to resistance to freezing. In other cases the improvement has been measured with conventional tests for soundness of aggregate using the crystallization of sodium sulfate or magnesium sulfate; the reliability of these tests has been the subject of active discussion [51].

It is to be expected that the influence of aggregate on frost resistance will be the object of extensive studies in the future, and more detailed information may now be obtained as the influence of the paste may be excluded by the use of adequate amounts of purposefully entrained air.

Freezing of Concrete at Early Ages

Hydraulic Pressure

In the preceding section a survey has been given of the different mechanisms of frost action in mature concrete. It has been shown that the hydraulic-pressure theory has been developed to a very high level of perfection, making it possible to give a satisfying explanation of how the entrained air bubbles are able to protect the paste of hardened concrete against freezing. On the other hand it has also been mentioned that the theory of macroscopic ice segregation seems to be more applicable to concrete in the fresh state.

Based upon studies of T. C. Powers and coworkers and some investigations in Europe, a survey of the change in freezing resistance of concrete during the hardening process will be given.

In 1949 Powers presented a model from which he developed formulas for the hydraulic pressure developed in paste during freezing [23]. At the RILEM Symposium in Copenhagen the author used this theory and model in order to discuss the change of the important factors in this formula during the hardening process, and a brief summary is given below [52].

The basis of this discussion was the following expression for the hydraulic pressure in air-entrained concrete, which is a stage in the development of the general formula, eq (1).

$$P=a\left(1.09-\frac{1}{s}\right)\frac{uR}{K}\left(\frac{L^3}{r_b}+\frac{3L^2}{2}\right)\text{ dynes/cm}^2 \quad (2)$$

where:

a=a factor, depending, among other things, on the viscosity of the water—g/cm sec.
s=saturation coefficient of the cement paste.
u=amount of water, in grams per gram of cement, which freezes when the temperature falls one degree—g/g °C.
R=rate of cooling, °C/sec.
K=permeability, cm^2.
r_b=average radius of air bubbles, cm.
L=spacing factor of air bubbles, cm.

The last part of the equation may be substituted by

$$f(L)=\frac{L^3}{r_b}+\frac{3L^2}{2}. \tag{3}$$

The formula has been derived under the assumption of entrainment of air bubbles, into which water can escape when the concrete freezes. If the hydraulic pressure, P, exceeds the tensile strength, T, of the paste, it will produce rupture. In the following the controlling factors of the formula are discussed.

The degree of saturation, s, of the cement paste has a very great influence on the hydraulic pressure. It will be seen from the formula that $s=0.917$ makes $P=0$, i.e., no hydraulic pressure will develop. The water, in this case, turns into ice within the voids without any movement of water being involved. In practice, evaporation and internal drying—self-desiccation—may, under favorable conditions, reduce the degree of saturation to 0.91 or less and no damage will occur in case of freezing. For degrees of saturation between 0.91 and 1.0 Powers has made a computation under certain assumptions which shows that already at a reduction of the degree of saturation to a value of 0.97 the hydraulic pressure will only be 56 percent of the maximum value. In all these considerations it is assumed that the water is homogeneously distributed throughout the paste, which is seldom the case.

The hydraulic pressure will increase with u, the amount of water freezing per degree drop of temperature. If freezing can be prevented, for example through addition of anti-freeze compounds, protection of the concrete will be attained. The concentration of these compounds generally recommended and used will afford protection only down to a few degrees below 0 °C.

In a discussion of freezing and thawing tests Powers [3] pointed out that supercooling might have a considerable effect upon the rate of ice formation, and mentioned tests carried out by Valore [15] at the National Bureau of Standards several years ago. This effect may be of great importance in investigations carried out in the laboratory, but on the other hand it is suggested by Powers that the same effect is not to be expected in actual structures where an ice layer is formed on the surface. This question is as far as the author knows, not clarified as yet.

The higher the rate of cooling, R, the higher the hydraulic pressure. The rate of cooling can be reduced through insulation of the concrete. The larger the ratio of the volume of the concrete to the area of the exposed surface the less the temperature of the concrete will be influenced by fluctuations of the outside temperature, and a lower rate of cooling will result. Heavy structures are in this respect less liable to damage by frost than are slender structures.

For actual structures the rate of cooling is furthermore determined by the prevailing climatic conditions during winter time. Consequently, the influence of this factor is determined not only by the structure's geographical location, but also from local topographical conditions, wind velocity, radiation to the sky, and so on.

Lower permeability, K, of the concrete involves higher hydraulic pressure. During hydration the permeability is reduced, and the resistance to frost, all other factors unchanged, will not increase with curing time. The permeability depends, moreover, on the qualities of the cement and it will increase with the w/c ratio.

The permeability of hardened portland-cement paste has been studied by Powers and Brownyard [53] and later by Powers, Copeland, Hayes, and Mann [54, 55, 56]. In the latest publications it is stated that the permeability is reduced to one third, approximately, when the temperature is reduced from 27 °C to a little above the freezing point. It was further found that the coefficient of permeability decreases about one order of magnitude a day for the first two to three days of curing at normal temperature.

Air Entrainment

The last part of eq (2) is related to the entrained air and its distribution into tiny bubbles. As already mentioned above, the possibility of relieving the stresses from the hydraulic pressure is dependent upon the distance between the bubbles rather than the amount of entrained air. In most of the theoretical computations carried out by T. C. Powers [23, 57], it is assumed that this spacing factor $\bar{L}$ is equal to 0.01 in. =¼ mm. In the latter reference, tables may be found to determine the air content necessary for different cement contents, water-cement ratios, and values of the specific surface of the voids.

Tensile Strength

The tensile strength of concrete will at lower degrees of hydration mainly be determined by the tensile strength of the paste, T. As already discussed above, internal damage will take place in the concrete if the hydraulic pressure exceeds the tensile strength of the paste. Dividing eq (2) by the tensile strength of concrete and inserting eq (3), we obtain

$$\frac{P}{T}=a\left(1.09-\frac{1}{s}\right)\frac{u\cdot R}{K\cdot T}\,\phi(L). \qquad (4)$$

If the concrete is exposed to a large number of freezing-and-thawing cycles, the hydraulic pressure should not exceed the fatigue limit of the concrete,

$$F=\beta T \qquad (5)$$

where β is a constant <1.

Hydraulic Pressure as Influenced by the Hardening Process

In eq (4) the following quantities are not influenced by the progress of the hydration, viz, a, which is a constant; R, the rate of cooling; and L, the spacing factor.

The factors following are dependent upon progress of hydration: s, the saturation coefficient; u, the amount of ice formed per degree drop of temperature; K, the permeability; and T, the tensile strength.

For evaluation purposes it may be assumed that in winter concreting in practice it is not always possible to prevent the access of water from melting snow and ice, and consequently the degree of saturation may be equal to 1.0. Hence the maximum hydraulic pressure $P_{\max}$ may be expressed by

$$\frac{P_{\max}}{T}=\gamma\,\frac{U}{KT}\cdot R\phi(L). \qquad (6)$$

where U is the value of u for saturated paste.

Powers has suggested in one of his papers [23] substituting for the three variable factors the parameter Z, equal to $\frac{K\cdot T}{U}$.

Expressing the left side of eq (6) equal to unity, the requirement for the distribution of the entrained air can be expressed by the following formula

$$\phi(L)_{\max}=\gamma\cdot\frac{Z}{R}. \qquad (7)$$

The author has in a previous paper [52] demonstrated that the factors K, T, and U can be estimated from a single variable, the nonevaporable water w_n. The derivation was based upon Powers and Brownyard's paper "The Physical Properties of Hardened Portland Cement Paste" [58] and the information available at that time [59]. For illustrative purposes figure 7 gives the result of these computations, each of the variables being drawn as a function of the nonevaporable water content, and it is shown that the parameter Z has a maximum corresponding to the highest degree of freezing resistance, when the hydration process has reached a stage where the nonevaporable water content for this specific mix is 0.15 g/g cement.

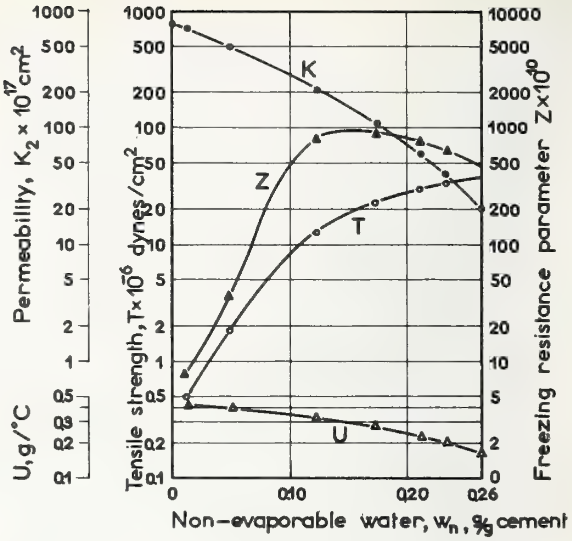

FIGURE 7. *Change of physical properties during hardening of cement paste.*

(Nerenst [52])

Adopting a certain amount of air and specific surface of the voids, it was computed that the Z value should be above 41×10^{-10} in order to obtain resistance to freezing with a specified rate of cooling of 3 °C/hr.

Assuming that damage would be caused by hydraulic pressure only, the necessary degree of hardening could by some further assumptions be converted into a requirement of development of a certain amount of heat of hydration, as a relation exists between the amount of nonevaporable water and the heat of hydration. This has been shown by Powers and Brownyard [60] and been confirmed by experiments carried out by Danielsson [25] in Stockholm.

From experiments Rastrup [61] had determined the relation between heat of hydration and time and temperature for Danish cements. These computations were used in working out recommendations for winter concreting in a Danish publication [10].

The results mentioned above are rather theoretical and based upon a great number of assumptions. Later experiments by Möller [4] to verify the computed prehardening times indicate that they are rather conservative for mixes of low water-cement ratio but seem to be too short for mixes with a water-cement ratio above 0.7 by weight.

The revised prehardening periods appear in table 3 for concrete made with Danish cement, assuming an air content of 4 percent and a cooling rate of 3 °C/hr.

It may be of interest to notice that since these recommendations were published in 1953, not a single case of failure has been reported to the Danish National Institute of Building Research from job sites where these recommendations have been followed.

Table 3. *Required prehardening for attainment of resistance to freezing.*

Air content L=4 percent (Nerenst, Idorn, and Rastrup [10])

Danish cement types	Cement content	Required prehardening in hours	
		at 0 °C	at 15 °C
	kg/m³	h_0	h_{15}
Standard portland	300	45	16
	225	49	17
Rapid-hardening portland	300	40	14
	225	43	15
Extra-rapid-hardening portland	300	34	12
	225	37	13

Macroscopic Ice Segregation

In presentation of the various theories which apply to concrete, the theory of macroscopic ice segregation has been mentioned. It is pointed out that this phenomenon is only observed in concrete of low quality or concrete in the first stage of hydration. In a paper presented at the RILEM Symposium in Copenhagen in 1956, Powers [13] mentioned an interesting theory worked out by Winterkorn [62] on the formation of ice lenses in systems with low tensile strength. Application of this suggestion to concrete would indicate that macroscopic ice segregation may be possible within the first two or three days of curing at normal temperature.

In his derivation of this time interval Powers seems not to take the increasing tensile strength of the cement paste into consideration. From soil mechanics it is known by experience that a certain load is able to prevent the formation of ice lenses. If this principle also applies to concrete, essentially shorter curing time should be necessary to prevent the formation of ice lenses.

In the discussion of an earlier report of Powers, Douglas McHenry and H. V. Brewer [12] presented a photograph of concrete showing ice segregation resulting from slow freezing of concrete at the age of 4 hr.

As it is of very great importance to determine the time interval in which macroscopic ice segregation is possible, detailed references are made below to observations made by Bernhardt [63] in Norway and Möller [4] in Sweden.

Bernhardt's Observations

In Bernhardt's [63] investigation Type I portland cement was used at water-cement ratios between 0.4 and 1.2. The concrete was poured at a temperature of +20 °C and placed in the freezer after varying prehardening times. The test specimens were 10-cm cubes, and when the specimens in the freezing series and the blank specimens had obtained the same degree of hydration the compressive strength was determined. After failure the broken specimens were investigated with the naked eye to determine the existence of ice needles.

For all specimens frozen immediately after manufacturing, ice needles were found. When the prehardening time was equal to 4 hr, evidence of the formation of ice needles was found in most cases. After 8 hr this phenomenon was observed in only very few cases. Bernhardt has drawn the conclusion that serious decrease in compressive strength is found only when there is clear evidence of the formation of ice needles. Bernhardt noticed that the ice needles were found mainly on surfaces of the coarse aggregate and suggested that the observed decrease in the compressive strength was caused by the reduction in bond between the aggregate and paste.

Möller's Observations

In Möller's experiments [4] the necessary prehardening time was determined from the modulus of rupture, the change in resonance frequency, and measurements of the dilation during freezing. On the formation of ice needles Möller reports that in four test series all characterized by a cement content of 240 kg/m³ of concrete and made with and without air entrainment and calcium chloride, a pattern of ice needles was found in all specimens with a prehardening time of 4 hr or less. After 8 hr the ice needles were found in one of the four mixes, which was characterized by having no addition of air-entraining agent or calcium chloride.

Whenever ice needles were found, the modulus of rupture and the modulus of elasticity were considerably decreased (10–15 percent). For four series of specimens with a cement content of 300 kg/m³ and water-cement ratio about 0.5, ice needles were found in specimens with a prehardening time of 4 hr at +20 °C or less.

Möller used two different procedures of freezing. In the first case the specimens were stored for a prolonged period in a freezing room at a temperature of −10 to −15 °C. In the second case the specimens were placed in a freezing room giving one cycle per day between −5.5 °C and +5.5 °C. In the latter case the temperature drop of the concrete is milder and smaller than in the first case and consequently the degree of the hydration when freezing starts will be a little higher for the specimens exposed to the cyclic treatment. It is interesting to notice that with the high cement content ice needles were found only in the specimens placed at low temperature. It is normally assumed that the formation of ice needles is favored by slow freezing, and it is difficult to explain the observed differences between the two cooling conditions. Möller reports the initial and final set of the cements employed as shown in table 4.

It may be seen that the formation of ice needles is possible after initial set but not later than the final set. It is readily admitted that the method of observation may have been too crude to obtain an exact fixing of the time necessary to prevent ice needles. Furthermore the absence of ice needles is no assurance that the concrete has not

TABLE 4. *Initial and final set for Swedish cements*
(Möller [4])

Cement brand	Setting time in hours and minutes	
	Initial set	Final set
G	3–35	9–10
N	2–50	7–30

The values refer to the use of the Vicat standard needle.

been damaged by the freezing, as emphasized by Möller.

Nerenst's Observations

A few observations made by the author in the field may be pertinent to this discussion of the formation of macroscopic segregation of ice.

In the top layer of a gravel pit it was observed about 10 years ago that on stones of the size 10–20 mm, layers of ice had been developed in thicknesses of up to 10 mm. The direction of growth was almost horizontal, i.e., perpendicular to the surface. It was also found that this formation only took place on aggregate with a porous texture. The particles were not investigated in detail, but they were of the type of lime-containing opal which has been causing a lot of trouble in Denmark on account of its reactivity with alkalies. The porosity might have been of the order of 10 percent by volume.

It is suggested that the process which had taken place was that during freezing a small amount of water was on the surface of the particles or perhaps reached the surface when the stone started to freeze. Once a layer of ice had been formed, it had the capability of extracting unfrozen water, as described for instance by Powers and Helmuth [6]. In the thin layer of water at the boundary between the ice and the particle it is suggested that the water is exposed to forces of adhesion which lower the freezing point. As long as the freezing rate is sufficiently low the freezing zone may be on the surface of the particle and water may be drawn from the capillary cavities in the particle passing through the boundary zone and converted into ice with the result that the ice lenses grow in thickness. The water is supplied from the particles proper and possibly from other grains behind the particles in question. It is to be noticed that similar observations could not be made on dense stone particles, for instance of granite, dense flint, etc.

In the second case a concrete floor had been placed in springtime without taking any special precautions, consequently the concrete temperature at placing may have been about +4–5 °C. The rate of hydration is rather low at this temperature, and when the air-temperature during the night dropped below the freezing point the surface of the floor was damaged in a peculiar way.

In the affected area a number of blisters were observed. By closer examination it was found that below each of these small blisters or mounds was a stone. These stones consisted of various proportions of lime and badly crystallized silica in the range from amorphous (opal) to cryptocrystalline structure (chert). By closer examination the author found that a very thin layer of mortar was lifted from the surface of the stone by individual ice lenses formed in the contact layer between paste and stone (fig. 8). In none of the cases were the stones damaged by the freezing. The thickness of the layer was 7–8 mm and as none of the stones had dimensions greater than 30 mm, it may be concluded that the water used for forming the ice lens was drawn not only from the particle proper but also from the surrounding mortar.

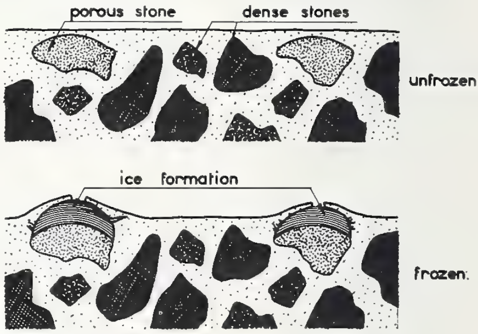

FIGURE 8. *Macroscopic ice segregation above porous stones in concrete floor frozen at an early age.*

These observations may be difficult to obtain by laboratory experiments as this special type of ice lens may only be developed under certain freezing conditions and in combination with a certain porosity and structure of the stone and degree of hydration of the surrounding paste.

Sandford's Observations

Some recently reported experiments in Sweden carried out by Sandford [64] on clay bricks are illustrative to the discussion of ice in porous materials. In order to get a better reproduction of the natural exposure of bricks to freezing action, each stone was separated from the other specimens by a separating layer of wet mineral wool.

The assembled framework was placed as the door to the freezing room, so that only one end was exposed to the cold air, and the other end to the room at a normal temperature.

When the air temperature of the freezing room was −5 °C, the freezing zone was situated only a few millimeters below the surface. After a certain period it was found that a body of ice was growing from the exposed cold surface and attaining a length up to 10 cm (fig. 9). This phenomenon was observed only on bricks with high resistance to freezing.

It was found very difficult to regulate the location of the freezing zone, and when freezing took place at greater depth than a few millimeters no protruding ice was observed. Application to the

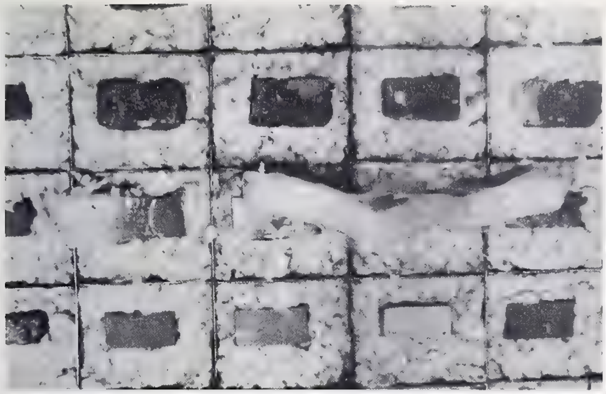

Figure 9. *Ice lenses formed on clay bricks during slow one-dimensional cooling.*

(Sandford [64])

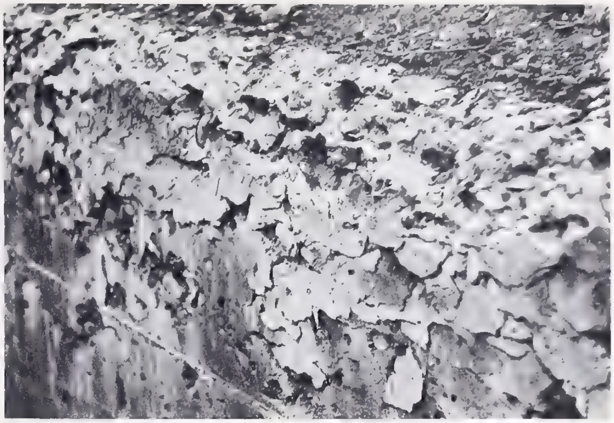

Figure 10. *Frost damage to green concrete containing porous aggregate.*

exposed surface of a paint with low bonding strength had the effect that the membrane was displaced by the protruding ice. Application of a thin layer with high bonding strength prevented the formation of ice on the outside, and rupture took place even in bricks which normally had a very high resistance to freezing. From this test Sandford concluded that bricks should not be treated with an oil paint, and we may have a demonstration of how the cement paste increases the risk of frost damage in saturated porous aggregate.

Some Danish Observations

It seems that the boundary layer between aggregate and paste is a locus for favorable conditions for the formation of ice needles up to a certain degree of hydration of the surrounding paste.

Danish concrete aggregate may contain various amounts of porous limestone and chert. The orgin and mineralogic properties have been studied and described by Søndergaard [65] in connection with the comprehensive investigation of alkali-aggregate reactions in Denmark. The permeability of these stones is not known and the following remarks are consequently of speculative nature.

The author observed ten years ago a concrete canal for a distant heating system. The maximum size of the aggregate was about 50 mm, and the cement content about 250 kg/m^3. The concrete was exposed to freezing after a prehardening period equivalent to 4–5 hr at 20°. As will appear from figure 10 the concrete was heavily damaged. The failure was mainly due to destruction of the bond between the porous aggregate and the paste.

The conclusion was drawn that in the very early ages of hydration this special material is able to extract water from the paste into the stone particle, from which water is supplied to the formation of ice coatings or ice needles in the boundary layer nearest to the freezing zone.

At later stages of hydration the permeability of the surrounding paste is decreased, and possibly also water is drawn from the particles to the paste during the self-desiccation period because, as pointed out by Powers [3], the pores in hardened portland cement paste are much smaller than the pores of most rocks.

This was confirmed at this job site because application of correct winter concreting methods which ensured a higher degree of hydration of the concrete before exposure to freezing gave a concrete with excellent appearance.

It may be mentioned that large amounts of aggregate with high contents of porous stone are used every winter with good results. Only under very severe exposures where the cement paste and later also the stones in the matured concrete are water saturated, the stone may be damaged by freezing causing the well-known pop-outs.

In January this winter the author studied a case where a great number of pop-outs were observed on the underside of a concrete deck above a cellar. Artificial heat was first supplied at an age of the concrete of 2 months because the contractor intended to apply a cement washing on the deck. No pop-outs were observed before the heating started and in the beginning it was difficult to explain where the additional moisture was supplied from, as the upper surface still was covered with snow, which by the way was an indication that the freezing zone was situated at some depth below the surface.

A closer study of the underside of the concrete revealed that water drops were condensing on the cold concrete, and it was assumed that the use of kerosene in the burners was one source of moisture as approximately one liter of water is created by the burning of one liter of kerosene. As the heating sources were moved several times during the work, it was concluded that the freezing zone may have been moving up and down in the concrete, which had been saturated to a critical degree during the heating periods.

The formation of ice lenses in the contact layer between paste and aggregate is shown in figure 11. The specimen is from a large concrete block with unknown time-temperature history before the freezing.

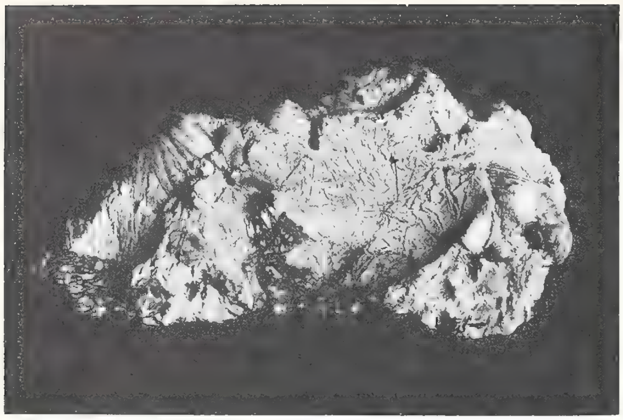

FIGURE 11. *Traces of ice needles in concrete with unknown time-temperature history.*

(Nerenst, Rastrup, and Idorn [10])

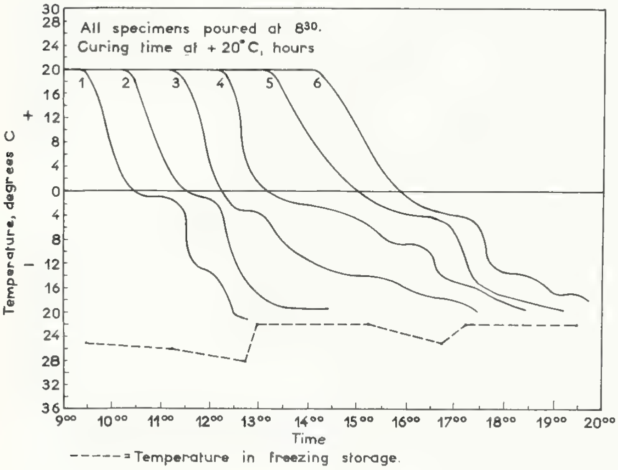

FIGURE 12. *Cooling curves of concrete beams with varying prehardening periods*

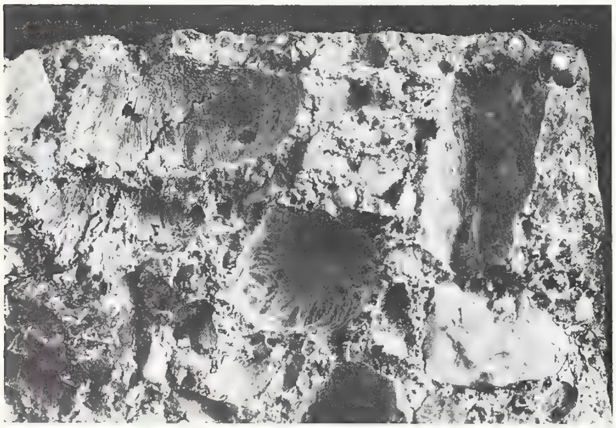

FIGURE 13. *Traces of ice needles in concrete frozen after 4 hr prehardening at +20 °C.*

(Curve 4, fig. 12)

The author has just started a few tests on the formation of ice needles in concrete at early ages. The concrete is cast at a temperature of +20 °C and placed in a commercial freezing storage of low temperature after varying prehardening intervals as shown in figure 12.

The temperatures are measured in the center of beams 10×10×60 cm in steel molds. The cooling curves are somewhat distorted because of heat of hydration, inaccuracies of measurement, and possibly changes in cooling conditions as the storage room has an intermittently working blower.

As an example of observations is shown figure 13, which corresponds to a piece of the beam, which had 4 hr prehardening.

To the author's knowledge, so far very little has been done in the laboratory to study how the direction of frost penetration and permeability of aggregate and paste, respectively, influence the orientation and amount of ice needles.

In the theories of cement paste it is assumed that the layer between air voids has a uniform temperature, which is justified from the small dimensions of the body. As the aggregate has much greater dimensions, the nonuniform temperature distribution may have considerable influence upon the direction of water movement.

The study is further complicated in paste with high amounts of water surrounding coarse aggregate with low porosity, as the heat released by the fusion of ice may delay the penetration of frost in the paste in comparison with the penetration of aggregate. Hence the hypothesis is put forward that coarse aggregate may serve as centers of low temperature, which may extract water from the unfrozen paste in all directions and thereby give rise to formation of rather thick coatings of ice in the early stages of hydration.

It is to be hoped that a well-equipped laboratory will study this problem in the future.

Necessary Prehardening to Avoid Damage From Freezing

Available information seems to indicate that the macroscopic ice segregation in green concrete is possible until the degree of hydration corresponds to a stage somewhere between initial and final set. On the other hand, the concrete may be damaged, even if ice segregation is not observed, and below a survey is given of some test results from laboratory experiments to determine the degree of hydration where concrete is undamaged by the first freezing. The presentation is largely based upon an unpublished report prepared by G. Möller [4].

Graf [66] in Germany made experiments on mortar specimens which were exposed to freezing at varying ages. The compressive strength was determined after thawing and additional curing. From his test results Graf drew the conclusion that concrete exposed for a very small number of freezing-and-thawing cycles should have a compressive strength of 80 kg/cm² before the first freezing. Concrete exposed to a great number of cycles of freezing-and-thawing should have obtained at least 150 kg/cm^2 before exposure. Kreüger in Sweden [67] also made experiments with mortar, and he concluded that concrete should be cured at least 24 hr at 20 °C before being exposed to first freezing. Some of his results are shown in figure 14. Both Graf and Kreüger made the tests on mortar and applied the results to concrete, which may not be correct because the contact layer between paste and aggregate is especially vulnerable to ice segregation.

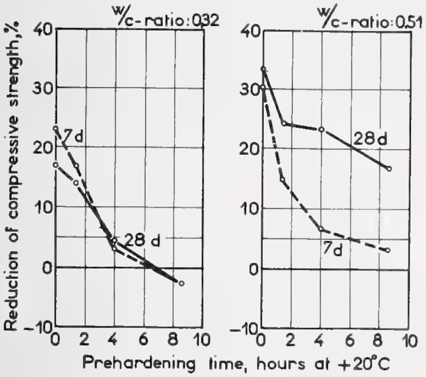

FIGURE 14. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens at two water-cement ratios.*

Tested after 7 and 28 days curing. Kreüger's results [67] as presented by Möller [4].

Scofield's Tests

Scofield [68] has carried out tests to determine the necessary prehardening. He expressed the compressive strength of frozen 15- × 30-cm cylinders as percent of the strength of normally cured specimens. For specimens placed in the freezing room immediately after manufacture, he found a reduction in compressive strength from 25 to 65 percent for portland cement. During the cooling period, the specimens obtained a maturity corresponding to 1½ to 2 hr curing at +20 °C. His test results are given in figure 15.

If we accept a compressive strength of 95 percent of that of the normally cured specimens as a criterion for no damage, it will be seen in the lower part of the figure that the necessary prehardening time for concrete with a water-cement ratio of 0.76 is between 12 and 17 hr. For the high water-cement ratio of 1.05 the necessary prehardening period is longer, i.e., from 48 to 60 hr. When the prehardening took place in the moist room, considerably longer periods were necessary as shown in the upper part of figure 15. The figure shows only the compressive strength after curing periods of 28 days or longer, where the effect of delayed hardening due to the low temperature is less important than at earlier ages. It will be seen that even after 96 hr curing at 21 °C the concrete with the water-cement ratio of 1.04 has not gained sufficient strength. In this case air entrainment has not been used, but the test results demonstrate very clearly that prehardening under conditions that permit a reduction of the degree of saturation is very beneficial for the concrete.

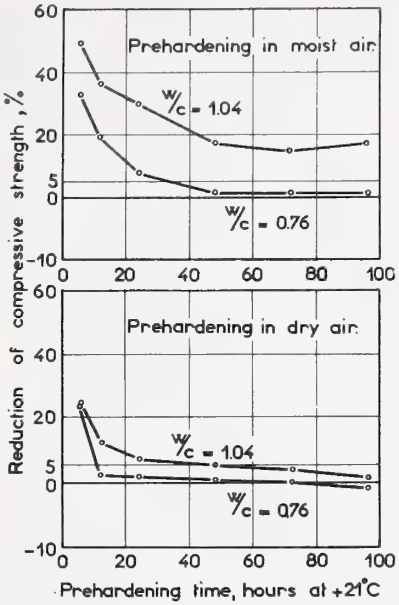

FIGURE 15. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens for two water-cement ratios and two curing conditions.*

Scofield's results [68] as presented by Möller [4].

McNeese's Tests

McNeese [69] has also carried out tests to determine the necessary prehardening time on non-air-entrained concrete. The concrete had a cement content of 275 kg/m^3. Portland cement Type I was used. The water-cement ratio was 0.6. The concrete had a slump of 7.5 cm (~3 in.) and no air-entraining agent was added.

Cylinders having dimensions $B=15$ cm, $H=30$ cm, were exposed to freezing after 0, 1, 3, and 6 hr of prehardening at +22 °C or +4.5 °C. Four different temperatures of freezing were used within the range of −4 to −26 °C, and the length of freezing was 3 days. The specimens were then cured in moist air at a temperature of +22 °C until the compressive strength was determined at ages 3, 7, and 28 days without taking into consideration the period during which the concrete temperature was below +10 °C. The test results were expressed as percentages of the strength of companion specimens cured at 22 °C. Möller has shown that the frozen specimens had obtained a little extra curing period corresponding to 5 hr at 22 °C.

McNeese's test results are given in figure 16 as presented by Möller. It will be seen that the lower freezing temperature seems to require a longer prehardening time. If we permit a reduction in compressive strength of 5 percent, the necessary prehardening time for this type of concrete seems to be between 8 and 12 hr.

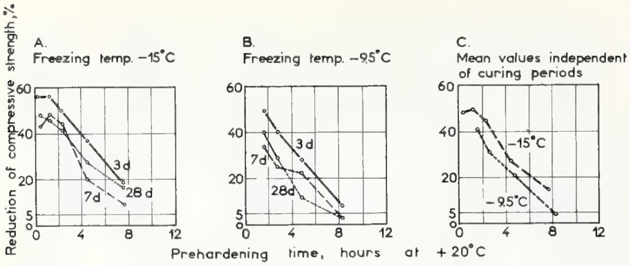

FIGURE 16. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens as influenced by freezing temperature and length of after-curing period in days.*

Water-cement ratio=0.6. McNeese's test [69] as presented by Möller [4].

Bernhardt's Tests

Bernhardt in Norway [63] carried out a comprehensive investigation including variation in water-cement ratio, consistency, amount of accelerators, air-entraining agent, freezing temperature, freezing period, curing period after freezing, and the prehardening period. The prehardening took place in air at +18 °C in the laboratory for 24 hours and later in moist air at +20 °C. His results have been treated by Möller as reproduced in figure 17. Applying the criterion of a permissible reduction of strength of 5 percent, the necessary prehardening time is about 8 hours for water-cement ratio 0.4 and increases to about 24 hr for the highest water-cement ratio of 1.0.

Bernhardt reached the conclusion that air entrainment did not have any beneficial effect on the resistance of concrete to early freezing.

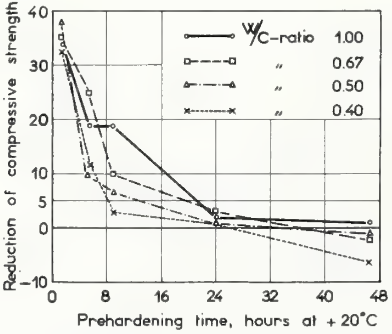

FIGURE 17. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens.*

Mean value of Bernhardt's test results [63] as treated by Möller [4].

Möller's Tests

A comprehensive investigation was carried out at the Swedish Cement and Concrete Institute by G. Möller in order to determine the necessary prehardening time for concrete exposed to freezing at early ages. The investigation was sponsored by the Swedish Institute of Building Research on account of the great economic importance to all the northern countries of establishing how the cost of concreting in winter can be reduced.

During the investigation extreme care was taken to test the specimens from the freezing series at the same degree of hydration as the blank specimens cured at normal temperature.

One type of maturity function has been proposed by Saul [70], Nurse [71], and Bergström [72]. In the maturity function developed by these authors it is assumed that hydration will take place even at a temperature down to −10 °C. The maturity is computed as

$$M=\Sigma(t+10)\cdot\Delta a_t \tag{8}$$

where $\Delta a_t=$ the curing time at the temperature t °C. This function has been modified by Nykänen [73].

A different way of computing the maturity or degree of hardening has been proposed by Rastrup [61], where the curing time a at a fixed temperature t may be computed from the formula

$$a=\Sigma 2^{\frac{t_v-t}{10}}\cdot\Delta a_v \tag{9}$$

where $\Delta a_v=$ the intervals of curing time at the varying temperature t_v. The different maturity functions were discussed at length at the RILEM Symposium in Copenhagen [13].

Although none of the proposed maturity functions take all the variables pertaining to cement hydration into consideration they seem to be of very great help in making comparisons between concrete specimens exposed to low temperature or a number of freezing-and-thawing cycles and the corresponding blank specimens cured at normal temperature. By the use of the Saul-Nurse-Bergström maturity function, G. Möller is able to exclude the influence of low temperature upon the strength development. Consequently, when expressing the strength obtained in the freezing series as percentage of the strength of normally cured specimens, a reduction is exclusively considered to be caused by the freezing damage.

In Möller's experiments the cement content varied between 200 and 300 kg/m^3, the water-cement ratio varied between 0.49–0.90, the consistency as measured by the slump test was 1–8 cm. The tests included series with and without air-entraining agent. In the latter case the air content was approximately 2–3 percent by volume. When air-entraining agent was used, the air content was 4.3–6.6 percent by volume.

As criteria of the freezing damage were chosen: (1), the reduction in the modulus of rupture in percent of that of normally cured specimens; (2), the reduction in dynamic modulus determined by resonance-frequency method; and (3), the dilation during freezing. For each mix the reduction in the modulus of rupture and dynamic modulus were plotted against the prehardening time in a similar way as shown in figure 17, and, applying the same level of permissible reduction in strength of 5 percent, the required prehardening time was determined.

The results are found in figure 18 together with all the previously mentioned tests. The required prehardening time is plotted against the water-cement ratio, which in Möller's opinion is the most decisive factor for obtaining early resistance to freezing. Taking into consideration that test conditions have varied with regard to cement type, fineness, curing, rate of cooling, and strength determinations, it must be admitted that the scatter of test results is not so high as could be expected.

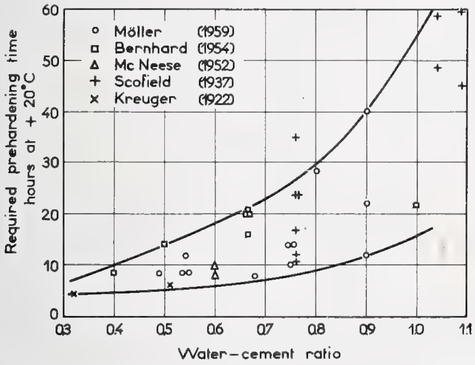

FIGURE 18. *Relation between the required prehardening period and the water-cement ratio.*

As presented by Möller [4].

Möller has computed the strength values which correspond to the required prehardening periods, determined by his own tests. He found that the required compressive strength is of the order of 25–30 kg/cm^2 and the modulus of rupture should be at least 5 kg/cm^2.

The effect of air entrainment was not very clearly demonstrated by the strength testing, as the observed reduction of the required prehardening time could be explained from the reduction of the water demand. The effect of the air was, however, very clearly demonstrated in the measurements of dilation.

The method used was to pour the fresh concrete in rubber balloons and determine the change of volume by the pycnometer method.

The test results are given for series A in figure 19. The concrete had a cement content of 200 kg/m^3, a water-cement ratio of 0.90 and the amount of entrapped air was 2.7 percent. The curves to the left indicate the dilation during the first cooling period from +20 °C to −5.5 °C and the numbers of the curves indicate the length of the prehardening period at +20 °C.

The diagram to the right indicates the relationship between the number of freezing and thawing cycles (−5.5 °C to +5.5 °C each day) and the remaining dilation after the specimen has been brought back to the +5.5 °C level. The values are not corrected for variation of the specific gravity of the pycnometer fluid (water-spirit mixture or ethylene glycol), but it is nevertheless possible to see that the dilation is diminishing with increasing prehardening time.

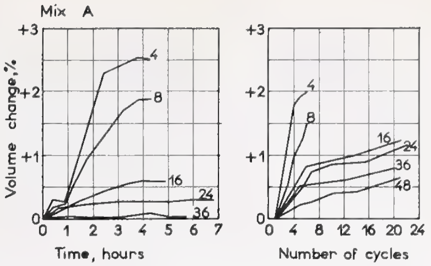

FIGURE 19. *Volume change of concrete during first cooling (left) and remaining dilation after cycles of freezing and thawing (right) after prehardening periods in hours at +20 °C as indicated on each curve.*

Non-air-entrained concrete (L=2.7%) of 200 kg cement/m^3 and w/c=0.90 (Möller [4]).

In figure 20 are given the results from a concrete with the same cement content as in figure 19. The amount of entrained air was 6.6 percent, and, as the water demand was reduced due to the entrained air, the water-cement ratio was 0.80.

By comparison of the two concrete mixes it is readily seen that the entrained air (fig. 20) reduces the dilation to one-fifth of the value obtained for the non-air-entrained concrete (fig. 19) for the testing after 4 hr prehardening.

The observations may be explained by the earlier-mentioned theories [6, 12, 23].

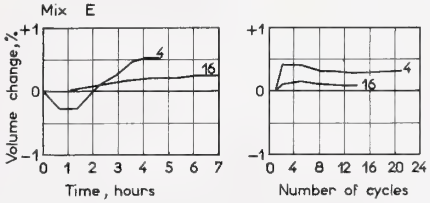

FIGURE 20. *Volume change of concrete during first cooling (left) and remaining dilation after cycles of freezing and thawing (right) after prehardening periods in hours at +20 °C as indicated on each curve.*

Air-entrained concrete (L=6.6%) of 200 kg cement/m^3 and w/c=0.80 (Möller [4]).

Johansen in Norway [74] made freezing tests on grouts for injection of cable ducts in post-tensioned concrete and found that the entrained air had a very beneficial effect in preventing expansion, when freezing took place after 3 days' curing at +5 °C.

Möller [4] has determined the relationship between the maximum increase in volume during the first freezing and reduction of the modulus of rupture (fig. 21).

From the reported data of decrease of the volume weight due to freezing in Graf's investigation [66], Möller has computed the permanent increase in volume and plotted these results against the reduction of compressive strength (fig. 22).

In both cases the reduction of strength is much greater than that corresponding to the increase of porosity.

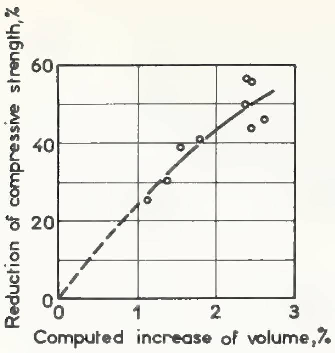

FIGURE 21. *Relation between the reduction of compressive strength in percent of that of normal cured specimens and computed remaining dilation.*

(Graf's results [66]) as presented by Möller [4].

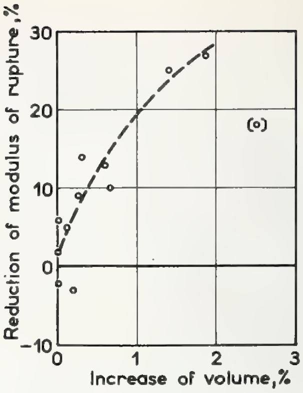

FIGURE 22. *Relation between the reduction of modulus of rupture and maximum dilation during the first cooling.*

(Möller [4])

Conclusions

Frost action in concrete has in many countries caused serious damage to exposed structures. Studies of the frost resistance of mortar and concrete have consequently been started in early periods of the concrete age, but it has not been the intention of the writer to give a historical review of testing procedures and the test results obtained in this early period.

The present paper is also incomplete insofar as many important reports on noteworthy developments may have escaped the writer's notice. This may especially be the case if the paper has been published in languages other than English, French, German, or the Scandinavian languages.

It cannot be avoided that selection of papers and the presentation of general principles and concepts are greatly influenced by the writer's own opinion on the subject. The theories and concepts which take full advantage of the highly increased knowledge of the basic physical properties of cement paste have a prominent place in the present review, although it has been almost impossible to present all these ideas in such a way that all the implications may be understood from this review. It is strongly recommended that the readers study the theoretical papers to which references have been made in the text.

It will be understood that the writer is in favor of using air-entraining agents in concrete structures exposed to freezing conditions, even if it has been possible in earlier days and may still be feasible to produce a concrete without air-entraining agent and still obtain a reasonable resistance to freezing under moderate climatic conditions. The incorporation of a reasonable amount of air, which is well distributed in the concrete, is, however, a very easy and economical way of obtaining a safeguard against frost damage which involves only small disadvantages if any with regard to reduction of strength. To obtain the full advantage of this—at least in Europe—relatively new development, recommendations of the mix design, control of air content, and the properties of air-entraining concrete should be prepared on a national scale based upon the climatic conditions prevailing, as the results from the laboratory tests should be adjusted to the actual climatic conditions. Tentative recommendations of this type were published in 1952 by the Danish Institution of Civil Engineers, and to the author's knowledge Denmark was the first country in Europe where an official organization accepted the use of air-entrained concrete for certain structures.

The air-entraining agents may be further developed, and the methods of mix design may be refined, but at the moment it seems that the resistance of hardened concrete now depends more than ever upon the properties of the aggregate, and further research is needed in this field. A few observations indicate that even dense stone and granite after crushing have been brought to such a state that the natural weathering process affecting all types of rocks may be accelerated after the incorporation of the particles in concrete, but no definite conclusions can be drawn as yet.

Freezing of concrete at early ages has recently been the subject of research in Scandinavia. Some relations between curing periods and resistance to freezing and thawing have been established, but further research is needed. No definite conclusions can be drawn with regard to the time at which macroscopic ice segregation will be prevented during the progressing hardening process. The influence of entrained air on frost action in concrete at early ages is still the subject of discussion.

The writer gratefully acknowledges the assistance given by several persons and organizations during the preparation of this paper.

The Portland Cement Association has sent me reports, which were difficult to obtain in Denmark. The Danish National Institute has supplied the photographs No. 1, 11, and 13 and among the staff members, Mr. N. M. Plum and Mr. Jørn Jessing have been specially helpful. Mr. Folke Sandford, Swedish Silicate Research Institute, has permitted the reproduction of figure 8. Mr. G. Möller, Gullhögen, has permitted the writer to draw freely on an unpublished report. Mr. C. Nymand made the drawings and Mrs. K. Steen Kristensen typed the manuscript.

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Discussion

R. A. Helmuth

A question of very great importance in research concerning frost action in concrete is how ice formation produces stresses in the porous structure of the hardened cement paste. According to the hydraulic pressure hypothesis (HPH), [1][1] freezing first fills all the pore space with ice and unfrozen water (actually aqueous solution), and then develops pressure which is generally prevalent throughout the pores in the paste, instead of producing stress concentrations at the frozen (larger) capillaries. As discussed in Poul Nerenst's excellent review paper, work in this laboratory led to the formulation in 1953 of an extended theory of freezing of water in hardened cement pastes and the protective effect of entrained air [2, 3]. This theory included two mechanisms: (1) the HPH, i.e., generation of pressures by ice formation and the relief of these pressures by saturated hydraulic flow to air voids, and (2) (osmotic) accretion of ice in capillaries and macroscopic segregation of ice in air voids by unsaturated flow. There are two unsaturated flow mechanisms: suction and surface diffusion. They are the result of free-energy differences between air-void ice and water and ice in the pores of the paste. Nerenst's review indicates that this extended theory represents "notable" progress, yet there have been several quite thorough studies since 1953 in which only the HPH is considered, no doubt because the mathematical formulation makes experimental results more amenable to analysis.

It is the purpose of this discussion to question whether saturated flow occurs in mature air-entrained cement pastes even in the early stages of freezing in pastes which are as nearly water-saturated as possible. This question is directly related to the question of how ice formation produces stresses. Stress concentrations resulting from saturated flow alone would be spaced according to the void spacing factors, which are about 0.25 mm or 250 μ in pastes with entrained air. On the other hand, stress concentrations at the sites of ice formation would be spaced according to the spacing of the capillaries, which in mature cement pastes are believed to be of the order of 0.01 μ in diameter and perhaps several times as far apart. According to the extended theory, dilation might be produced during saturated flow because of the hydraulic pressure and during unsaturated flow by highly localized osmotic pressures at the sites of ice formation. That the flow is almost entirely unsaturated even during the early stages of freezing will be shown using both the older data on which the extended theory was based and more recently obtained data.

Effect of Entrained Air Voids on Freezing Expansions

Examination of the formulation of the HPH reveals that the variables s, the saturation coefficient, U, the rate of ice formation, R, the rate of cooling, and $\overline{L}$, the void spacing factor, are variables that control the pressure and dilations during freezing. Experimentally both s and U are apt to be difficult to control because of moisture distribution changes produced by temperature change [4] and capillary size restrictions on ice formation [5]. Therefore, tests of the hypothesis should be designed to vary only R or $\overline{L}$ with s and U held constant. The most easily reproduced value of s is unity. This can be obtained if the paste is cured in water at the freezing temperature, or if the air voids contain free water that may be absorbed by the paste to maintain saturation in cooling from the curing temperature to freezing temperatures. Present consideration will be confined to results for pastes having only rather high air contents because pastes of low air content became somewhat desiccated as a result of cooling from room temperature, whereas high air content pastes with water in the air voids apparently remained water-saturated in cooling to freezing temperatures. Furthermore, the pastes of high air content and therefore small void-spacing factors, showed only relatively small expansions which were probably almost completely elastic.

An example of the kind of results obtained is given in figure 1, which shows a complete cooling-warming cycle for a paste with small void-spacing factor. Many tests of this kind were made. In every case the beginning of freezing is indicated by an expansion and temperature rise (or temporary cessation of cooling) caused by release of latent heat of fusion. Inspection of the curves reveals that subsequent length changes are functions of paste characteristics, air-void-spacing factor, and cooling rate.

Summary plots of most of these freezing curves are presented in figures 2, 3, and 4, which show the effect of variation of void spacing factor. The expansions produced by freezing are seen to yield to shrinkage at a rate much greater than the thermal contraction of the paste at temperatures above freezing, which indicates that the paste has been dried internally by accretion of ice in the air voids. A line of slope $35\times10^{-6}/°C$ has been drawn through the origin in each of these plots to show how closely the curves of small spacing factors approach this line. This close approach occurs regardless of paste porosity, except for the very impermeable pastes of $w/c=0.45$ in which these cooling rates must have been so high that the shrinkage appreciably lagged the changing temperature.

This shrinkage during freezing is taken as positive evidence that the flow of moisture to air voids at low temperatures is *unsaturated* flow.

The possibility of *saturated* flow to air voids in the early stages of freezing will also be examined.

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[1] Figures in brackets refer to the literature references at the end of this paper.

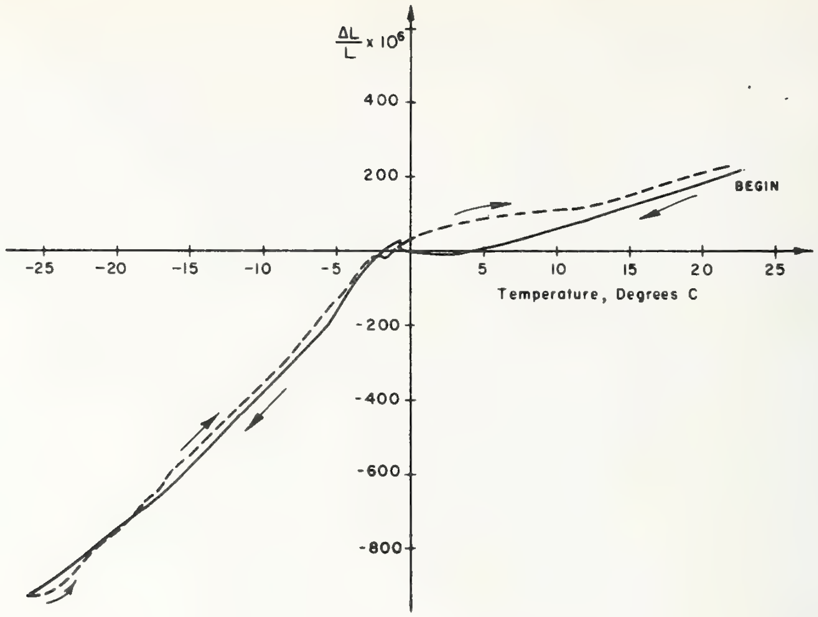
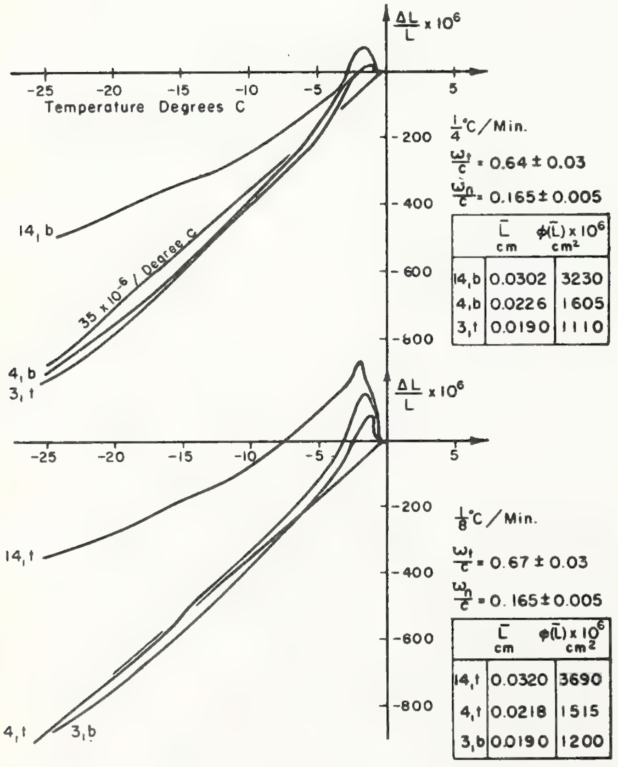


FIGURE 1. *Freezing-cycle test of specimen 4_1 b.*

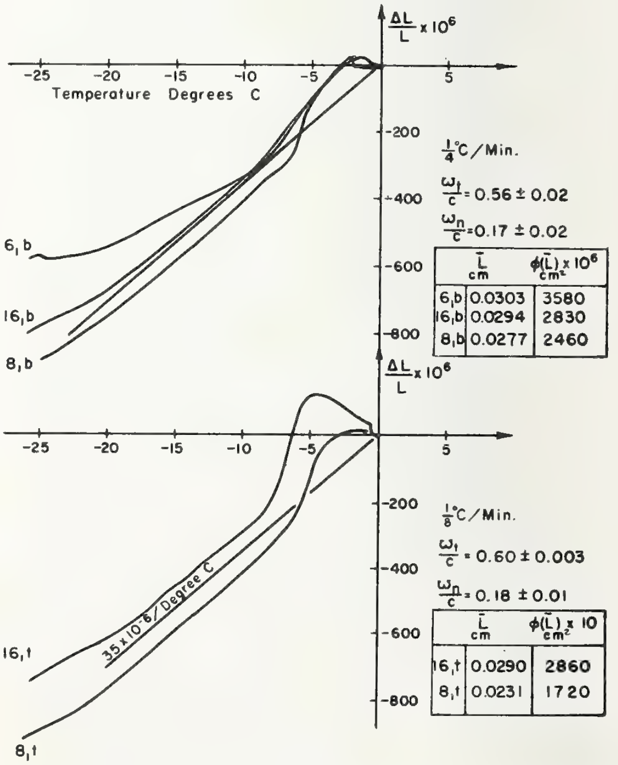
w_t/c was 0.669; w_n/c was 0.161; 14.8 percent air with a void-spacing factor of 0.0226 cm and ϕ (L)of 1605 cm². Cooling and warming at 0.25 °C per min.



	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
14, b	0.0302	3230
4, b	0.0226	1605
3, t	0.0190	1110

	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
14, t	0.0320	3690
4, t	0.0218	1515
3, b	0.0190	1200

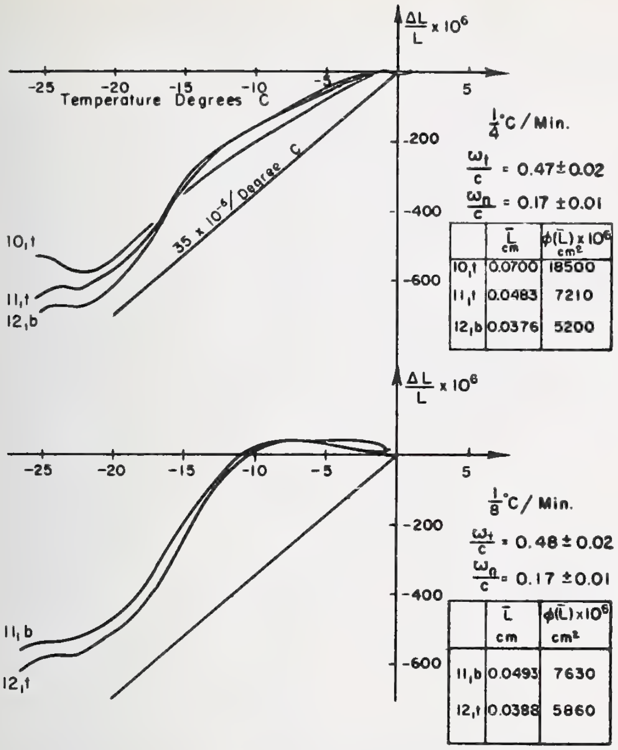
FIGURE 2. *Effect of spacing-factor variation in high-porosity pastes.*



	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
6, b	0.0303	3580
16, b	0.0294	2830
8, b	0.0277	2460

	$\bar{L}$ cm	$\phi(\bar{L}) \times 10$ cm²
16, t	0.0290	2860
8, t	0.0231	1720

FIGURE 3. *Effect of spacing-factor variation in medium-porosity pastes.*



	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
10,t	0.0700	18500
11,t	0.0483	7210
12,b	0.0376	5200

	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
11,b	0.0493	7630
12,t	0.0388	5860

FIGURE 4. *Effect of spacing-factor variation in low-porosity pastes.*

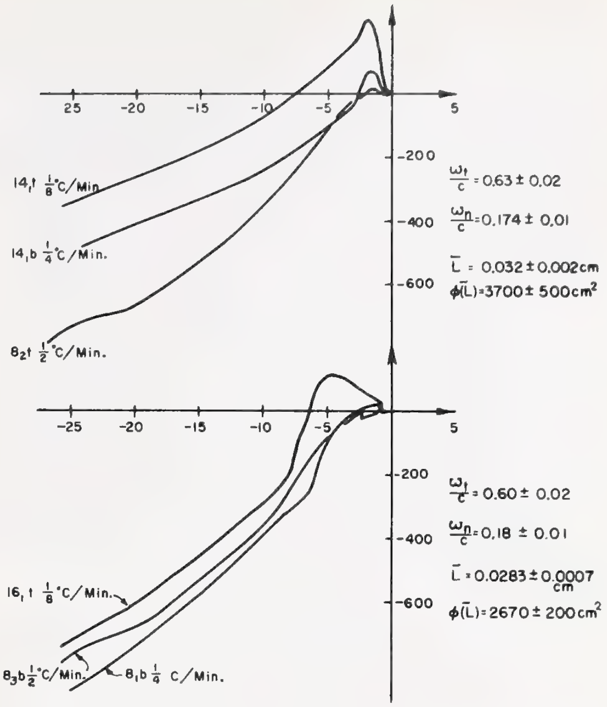


FIGURE 5. *Effect of rate-of-cooling variation on freezing expansions.*

In Powers' formulation of the hydraulic pressure hypothesis it was shown that for constant paste characteristics, the rate of cooling R and the spacing factor function $\phi(\bar{L})$ determined the maximum pressure generated by freezing the paste. As $\phi(\bar{L})$ or R increase, the maximum expansion should also increase. The results shown in figures 2, 3, and 4 are in accord with the deduction that the maximum expansion increases with the spacing factor function $\phi(\bar{L})$. Figure 5 gives plots of results at approximately constant paste characteristics and void spacing factors at three cooling rates. The top set of curves shows that for pastes of $w_t/c=0.63\pm0.02$, $w_n/c=0.174\pm 0.01$ and $\bar{L}=0.032\pm0.002$ cm, the maximum expansions *decrease* as the cooling rates increase. When $w_t/c=0.60\pm0.02$, $w_n/c=0.18\pm0.01$ and $\bar{L}=0.0283\pm0.0007$ cm as in the lower set of curves the same is true of the maximum expansions, though the behavior at lower temperatures results in contractions not related in the same way, probably because the cooling rate of specimen 8_1b dropped considerably below the nominal ¼ °C/min in the vicinity of −6 °C and this permitted more shrinkage than would have occurred with better control.

At the highest cooling rate used, ½ °C/min, the freezing expansion is almost completely absent in both sets of curves. This would be decisive evidence against the HPH if it were not for the fact that during cooling before freezing, moisture tends to move into the gel from capillary cavities in the paste, thus reducing the capillary saturation coefficient and the freezing expansion. When the air voids contain some water (as in all of these specimens) the paste can imbibe water from these voids and remain saturated during cooling, but this process takes time and if cooling is rapid it is possible some "desiccation" may result, even with water in the air voids. However, the differences in capillary saturation coefficients in these six specimens at the beginning of freezing are believed to have been very small because each began the progressive freezing expansion at a temperature much higher than comparable air-free pastes which could not imbibe water from air voids during cooling. For this reason these results are taken as strong evidence that no saturated flow occurred in these tests.

Though the expansions of pastes with entrained air vary qualitatively with void spacing factor as would be expected from either mechanism, the freezing expansion results with rate of cooling variation at constant void-spacing factor indicate that the expansions are limited by a mechanism different from that of freezing in place and saturated flow to air voids. The results are in accord with the theory of osmotic accretion by unsaturated flow.

In 1953 we believed that in the early stages of freezing, when ice formation was rapid, saturated flow of water occurred so easily that no appreciable pressures or dilations were produced. Then we could explain the observations without abandoning the HPH, which seemed to us too reasonable to deny. However, it seems now that not only these results can be explained without assuming saturated flow but that there are other results which indicate that the dilations must be produced only by stress concentrations at the sites of ice formation. These results show that expansions are produced in pastes free of entrained air even when there is ample empty space in the capillaries to accommodate the excess volume produced by ice formation.

Initial Formation of Ice in Slightly Supercooled Air-Free Pastes

In a paper [5] supplementary to Nerenst's review paper, the initiation of ice formation in the capillaries of hardened cement paste is discussed in some detail. There it is shown that the water in the pores supercools unless it is seeded by ice crystals. When it is seeded at sufficiently low temperatures, there is rapid freezing of a small amount of water, w_f. This amount can be estimated readily from the observed temperature rise ΔT_f, and the specific heat of the paste, C_p.

If the water that freezes in the capillary spaces undergoes the same volume change as pure bulk water does when it freezes, the volume change of ice formation is

$$\Delta V_i = 0.09\ w_f. \tag{1}$$

This volume change may then be compared with the fraction of the capillary space which is empty. If ΔV_i is greater than the volume of the empty capillary space, ice formation should develop pressure in the capillary water, at least in the capillaries where freezing occurs. Such pressure should expand the paste structure more than the thermal expansion alone.

The volume of the empty capillary space in the paste can be calculated from the fraction of the capillary space which is filled with water, or the capillary saturation coefficient, s_c, for pastes cured in certain ways. For self-desiccated pastes Copeland and Bragg's [6] work yields:

$$s_c = \frac{0.99 w_c}{0.99 w_c'} = \frac{w_o - 1.74 w_n}{w_o - 1.49 w_n} \tag{2}$$

in which 0.99 is the specific volume of the capillary water, w_c is the mass of the capillary water, w_c' is the mass of the capillary water for the paste when water-saturated, w_o is the mass of the original water, and w_n is the mass of the nonevaporable water. The fraction of the capillary space which is empty before freezing is then $(1 - s_c)$.

In the supplementary paper [5] some results of freezing experiments with self-desiccated pastes are presented (figs. 5, 9, 10, and 11 of that paper), in which the initial ice formation could not have filled all the available capillary space, yet sustained expansions occurred in these unsaturated pastes. In table 1 the volume increase produced by the amount of ice formed in the initial freeze is compared with the volume of empty capillary space for three specimens which showed definite expansions at the initial freeze. The w_f values were given in the supplementary paper. The volume increase was calculated from w_f and eq (1), then expressed relative to the volume of capillary space, 0.99 w_c', and also relative to the empty capillary space, 0.99 w_c' $(1 - s_c)$. In all three cases the ratio of the volume increase of ice formation to the volume of empty capillary space is much less than unity. Nevertheless, these freezes produced expansion not only during the initial freeze, but sustained expansions with further cooling. It seems necessary to conclude that the expansion after the initial expansion occurred because of lateral growth of the original dendrites, or some other slower form of crystal growth, in the initially frozen capillaries even when there was considerable empty capillary space in the paste. That is, the expansion was not produced by a generally prevalent pressure in all of the evaporable water in the paste, but was a result of local pressures produced in the capillaries where freezing occurred. This seems to be true even in the water-soaked pastes, in which we must take account of the transfer of moisture from capillary space to gel pores that occurs during cooling to freezing temperatures. The reduced value of s_c resulting from moisture movement from capillary spaces to the gel during cooling of these specimens to 0 °C from room temperature was calculated from [5]:

TABLE 1. *Comparison of the volume change of initial ice formation with available volume in self-dessicated pastes*

Specimen	s_c	$\frac{0.09\ w_f}{0.99\ w_c'}$	$\frac{0.09\ w_f}{0.99\ w_c'(1-s_c)}$
51_2b	0.989	0.00132	0.12
52_1t	.953	.00097	.02
55_2t	.940	.00063	.01

$$s_c = 1 - \frac{0.0194 w_g' + 0.0024 w_c'}{w_t' - 1.74 w_n} \tag{3}$$

in which w_g' is the water content of the gel when saturated, and w_t' is the total water content of the paste when saturated. This reduction of the capillary saturation coefficient is more than enough to accommodate the excess volume generated in the initial freeze, which is shown in table 2 for a group of water-soaked pastes, cited in the supplementary paper.

TABLE 2. *Comparison of the volume of initial ice formation with available volume in water-soaked pastes*

Specimen	s_c	$\frac{0.09\ w_f}{0.99\ w_c}$	$\frac{0.09\ w_f}{0.99\ w_c\ (1-s_c)}$	Initial Expansion$\times 10^6$
63_2t	0.9944	0.0017	0.30	120
60_2t	.9929	.0005	.07	26
61_1t	.9917	.0000	.00	0
57_1t	.9863	.0000	.00	3
59_1t	.9833	.0008	.05	50

These specimens were cured in water at 5 °C, but in preparation for the test they were in contact with water at about room temperature. At the time the tests were made it was believed that though the equilibrium water content of the specimens would be lower at room temperature than at 5 °C, it would require many hours for the specimen to lose an appreciable quantity of water when warmed to room temperature after curing at 5 °C. It was later discovered by weighings at 0 °C, 5 °C, and 25 °C that this change occurred rapidly. Hence it is believed that the water contents of these specimens were those required for saturation at 25 °C and not at 5 °C. Even if this is only approximately true, the results of these calculations indicate that there was much more empty space in these pastes than necessary to accommodate all the excess volume produced by ice formation in the initial freeze, yet there immediately followed large progressive expansions.

The data in tables 1 and 2 indicate that stress concentrations at the sites of the initial ice formation are responsible for the dilations because the amount of ice formed was too small to fill all the pore space with ice and water. Confidence in this interpretation is enhanced by the rather good correlation in table 2 between the initial expansions and 0.09 $w_f/0.99\ w_c$, regardless of the amount of empty space.

Conclusions

The results presented above indicate that the expansion-producing mechansim in moist, hardened pastes, both with and without entrained air, is *not* the development of pressure in the water in all the pores, but is the production of localized osmotic pressures at the sites of ice formation. This appears to be true not only in the later stages of freezing, as shown in 1953, but even in the early stages.

The results with mature pastes containing entrained air showed no dilations caused by hydraulic flow. Nevertheless, it could be argued that saturated flow to air voids did occur, but with such little resistance that no dilations due to hydraulic pressure occurred. However, results with air-free pastes showed that dilations were observed even when the paste was unsaturated; therefore, saturated flow to even the much more closely spaced empty capillaries cannot occur so easily that no dilations result. Hence, when dilations are prevented, it must be because the pastes are even more unsaturated. This must mean that in the tests of pastes containing entrained air, unsaturated flow to air voids occurred early enough and to such an extent that positive pressures and saturated flow did not develop.

The reasons for the lack of saturated flow are: (1) the lack of water-saturation, which is caused by (a) the drying effect of ice in air voids [2] at temperatures below 0 °C, (b) self-desiccation caused by hydration of cement during curing, and (c) "cooling desiccation" resulting from moisture absorption by the gel during cooling to freezing temperatures; and (2) the very limited amount of freezing *in situ* that can occur during cooling because of capillary size restrictions on ice formation in the pores of the paste. These effects combine, in moist pastes with small void spacing factors, to dry the pastes before freezing can produce positive pressures and saturated flow of the water in the paste surrounding the air voids. Therefore, the dilations result from accretion alone, and the flow is unsaturated flow to capillary ice and air-void ice.

The above conclusions are based primarily on data obtained with water-soaked pastes of normal porosities with entrained air. Further investigation may reveal that hydraulic pressure is an important factor in the production of dilations (and saturated flow) in pastes without entrained air, in pastes of abnormally high porosity, or in immature cement pastes. Though we have made no thorough study of this question using immature pastes, a limited amount of available data for pastes with and without entrained air suggests that the above conclusions are also valid when as little as 20 percent of the cement is hydrated.

References

[1] T. C. Powers, The air requirement of frost-resistant concrete, Proc. Highway Research Board **29,** 184–211 (1949).

[2] T. C. Powers and R. A. Helmuth, Theory of volume changes in hardened portland cement paste during freezing, Proc. Highway Research Board **32,** 285–297 (1953).

[3] G. Pickett, Flow of moisture in hardened cement paste during freezing, Proc. Highway Research Board **32,** 276–284 (1953).

[4] R. A. Helmuth, Dimensional changes of hardened portland cement pastes caused by changes of temperature, to be published in the Proc. Highway Research Board **60** (1961).

[5] R. A. Helmuth, Capillary size restrictions on ice formation in hardened portland cement pastes, this Symposium, paper VI–S2.

[6] L. E. Copeland and R. H. Bragg, Self-desiccation in portland cement pastes, Am. Soc. of Testing Materials Bull. **204,** 34–39 (1955).

Discussion

Ulf Danielsson

In the principal paper "Frost Action in Concrete," Nerenst has made an excellent review of this complex field. However, I should like to comment upon one minor point. The equations given for the maximum hydraulic pressure set up at freezing contain the factor $\left(1.09-\frac{1}{s}\right)$, where s is the coefficient of saturation. A closer examination of the case of partial saturation shows, however, that the coefficient s should appear in the equations in a less simplified form.

In the paper "The Frost Resistance of Cement Paste as Influenced by Surface-Active Agents" [1] a formula for the rate of generation of water volume by freezing has been derived:

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[1] U. Danielsson and A. Wastesson, The frost resistance of cement paste as influenced by surface-active agents, Swedish Cement and Concrete Research Institute, Proceedings No. 30, 40 pp. (Sweden. 1958).

$$\mathscr{H}=\left(\frac{1}{\gamma_f}-\frac{1}{\gamma_w}\right)\left(-\frac{dz}{dT}\right)\left(-\frac{dT}{dt}\right)\frac{\gamma w_w}{(1-A)(1+w_0)}, \quad \text{(A)}$$

where:

$\mathscr{H}$=rate of generation of water volume by freezing, cm³ water/cm³ paste and sec.,

γ_f=density of frozen water, g/cm³ ($\gamma_f=0.917$ g/cm³),

γ_w=density of unfrozen freezable water, g/cm³ ($\gamma_w=1.000$ g/cm³),

z=weight ratio of frozen water to freezable water at temperature T,

T=temperature, °C,

t=time, sec.,

γ=density of the paste including air pores, g/cm³,

w_w=total weight of freezable water per unit weight cement,

A=total volume of air pores per unit volume of paste, and

w_0=water-cement ratio of the paste.

In the case when the paste is unsaturated before freezing starts ($s<1$), $\mathscr{H}$ is zero until the voids have been filled. This occurs when $z=z_0$, where:

$$z_0=\frac{\gamma_f}{\gamma_w-\gamma_f}\left(\frac{1}{s}-1\right). \quad \text{(B)}$$

Equation (A) is thus valid only in the range $z_0 \leq z \leq 1$. The maximum value for $\mathscr{H}$ is generally obtained at temperature T_0, corresponding to $z=z_0$, and we obtain:

$$\mathscr{H}_{\max}=\left(\frac{1}{\gamma_f}-\frac{1}{\gamma_w}\right)\left(-\frac{dz}{dT}\right)_{z_0}\left(-\frac{dT}{dt}\right)_{T_0}\frac{\gamma w_w}{(1-A)(1+w_0)} \quad \text{(C)}$$

where z_0 and T_0 depend on the saturation.

From eq (B), and with the condition $z \leq 1$ it follows that the water flow vanishes when the saturation is below $s=\frac{\gamma_f}{\gamma_w}=0.917$. The factor $\left(1.09-\frac{1}{s}\right)$ becomes zero for the same limiting value. Also in the case of saturated paste ($s=1$), there is agreement between eq (C) and that part of eq (2) in the paper under discussion corresponding to the source of the flow.

When, however, the saturation lies between 0.917 and 1, it is tacitly assumed in eq (2) that the function expressing the strength of the source, or the hydraulic pressure, is a linear function of $1/s$, which is not necessarily correct. The general behavior is given by eqs (B) and (C). Admittedly, in experimental work one usually tries to keep the test specimens saturated, but unsaturated conditions are often met with in practice, and therefore I feel that it is worth while to point out this inconsistency.

(Ed. note: *Because of the illness of its author, the above discussion was not submitted in time to permit a response by the author of the paper under discussion.*)

Paper VI–S1. Deterioration of Cement Products in Aggressive Media*

J. H. P. van Aardt

Synopsis

The chemical and compound compositions of various hydraulic cements are discussed in relation to chemical attack. Data are presented in regard to the corrosion of hardened hydraulic-cement mortars in aggressive media, such as solutions of sulfates and chlorides, acids, and soft waters.

In the corrosion of cement mortars in sulfate, chloride, and other salt solutions, the nature and the function of the cations in the systems are important. The behavior of mortars made with different hydraulic cements is compared, and it is shown that the state of equilibrium and curing have marked influences on the resistance of cement mortars to aggressive agents; the effects of high- and low-pressure steam curing, curing under water, and curing in humid atmospheres are discussed. The carbonation of mortars made with portland cement is found to be beneficial, and the substitution of a calcareous aggregate for a siliceous aggregate improves the resistance of cement mortars to sulfuric acid attack. High density and low permeability in mortars reduce their vulnerability to corrosion, and it is stressed that good quality of the mortar is of prime importance in any corrosive environment. Bad practice in this respect can outweigh improvements aimed at by the use of more corrosion-resistant cements.

Résumé

La composition chimique d'oxydes et de composés de différents ciments hydrauliques est discutée par rapport à l'attaque chimique. Des données sont présentées en ce qui concerne la corrosion de mortiers durcis de ciment hydraulique en milieux agressifs, tels que les solutions de sulfates et de chlorures, les acides et les eaux douces.

Quand on étudie la corrosion des mortiers de ciment dans les solutions contenant le sulfate, le chlorure et des autres sels, la nature et la fonction des cations dans les systèmes sont importantes. Le comportement des mortiers confectionnés de différents ciments hydrauliques est comparé, et l'on voit que l'état d'équilibre et de conservation ont des influences marquées sur la résistance des mortiers de ciment aux agents agressifs. Les effets de conservation à la vapeur sous haute et basse pression, la conservation sous l'eau et la conservation en atmosphères humides sont discutées. On trouva avantageuse la carbonatation des mortiers confectionnés de ciment portland et la substitution d'un agrégat calcareux à un agrégat siliceux améliore la résistance des mortiers de ciment contre l'attaque de l'acide sulfurique. Une haute densité et une basse perméabilité dans les mortiers réduisent leur aptitude à la corrosion et on souligne la première importance de bonne qualité des mortiers en tout milieu corrosif. A cet égard une mauvaise pratique peut l'emporter sur les améliorations recherchées par l'emploi de certains ciments résistants à la corrosion.

Zusammenfassung

Die chemische Zusammensetzung und die Verbindungen, die man in den verschiedenen hydraulischen Zementen findet, werden in ihrer Beziehung zu chemischen Angriffen besprochen. Angaben der Korrosion erhärteter hydraulischer Zementmörtel in zerstörenden Medien, wie Sulfat- und Chloridlösungen, Säuren und weichem Wasser, werden angegeben.

Bei der Korrosion der Zementmörtel in Sulfat-, Chlorid- und anderen Salzlösungen ist die Natur und die Wirkung der Kationen in den Systemen von großer Bedeutung. Das Verhalten von Mörteln, die aus verschiedenen hydraulischen Zementen hergestellt worden sind, wird verglichen, und es wird gezeigt, daß der Gleichgewichtszustand und das Aushärten einen großen Einfluß auf den Widerstand der Zementmörtel gegen angreifende Mittel haben; die Wirkungen des Aushärtens mit hoch- und niedriggespanntem Dampfe, unter Wasser und in einer feuchten Atmosphäre werden behandelt. Die Einwirkung der Kohlensäure auf Mörtel, die mit Portlandzement hergestellt worden sind, muß als wertvoll bezeichnet werden, und die Einführung eines Karbonataggregats an Stelle eines Silikataggregats verbessert den Widerstand der Zementmörtel gegen Schwefelsäureangriff. Ein hohes spezifisches Gewicht und eine niedrige Permeabilität der Mörtel macht diese weniger korrosionsanfällig; es wird betont, daß in einer korrodierenden Umgebung eine gute Qualität des Mörtels die Hauptsache ist. Wenn man hier falsch verfährt, kann man alle Verbesserungen, die durch die Anwendung korrosionswiderstehender Zemente hervorgebracht worden sind, wieder zunichte machen.

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* Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the South African Council for Scientific and Industrial Research, Pretoria, S.A.

Introduction

The main object of this paper is to show how various chemical and physical factors influence the durability of cement products and how diverse studies have contributed towards improved durability and greater usefulness of such products. The heterogeneous mixture of cement, water, and aggregate is a very complicated one, and it is not surprising that many conflicting data and observations concerning resistance to aggressive conditions are to be found in the literature. Slight variations in materials, methods, and experimental conditions can lead to major differences in results and conclusions. For this reason close control of variables and clear descriptions of experimental procedures and conditions are essential.

The corrosion of cement products is influenced not only by the chemical composition of the components but also by their physical state and nature, and hence it is a field of study involving chemistry and physics, as well as applied technology.

General Discussion on Chemical Composition in Relation to Chemical Attack

Susceptibility of Various Cement Compounds to Attack

It has long been known that the behavior of cements in aggressive media is largely determined by their compound composition. Thus it is now well established [1, 2, 3, 4, 5][1] that the C_3A content of portland cement determines its resistance to solutions containing sulfate ions, in that cements with low C_3A contents are more resistant than those with high C_3A contents. Often experimental results do not show a linear relationship between C_3A content of portland cement and the resistance of the cement products to attack by sulfates, but this lack of correlation is probably due to errors in estimating the C_3A content [6] and to the effect of physical factors such as density and permeability.

The reaction of sulfates with other constituents of portland cement has also been investigated [7, 8, 9, 10]:—C_4AF is found to be vulnerable to sulfates but to a lesser extent than C_3A, and, furthermore, crystalline C_4AF is reported to be more resistant than C_4AF in the glassy state. In addition it has been shown that the hydrates of the silicates, C_3S and C_2S, are more resistant to sulfate attack than those of C_3A and C_4AF.

Influence of Equilibrium Conditions on the Nature of Hydrated Cement Compounds

When anhydrous cement compounds are brought into contact with water, reaction and decomposition take place with the formation of hydrates. Supersaturated and unstable solutions are formed which slowly tend to equilibrium. However, when the mass sets and hardens, the mobility of the various ions is reduced and the attainment of equilibrium is very slow. For instance, figure 1 shows a neat cement specimen in which unhydrated particles of cement are still present after 28 days curing under water.

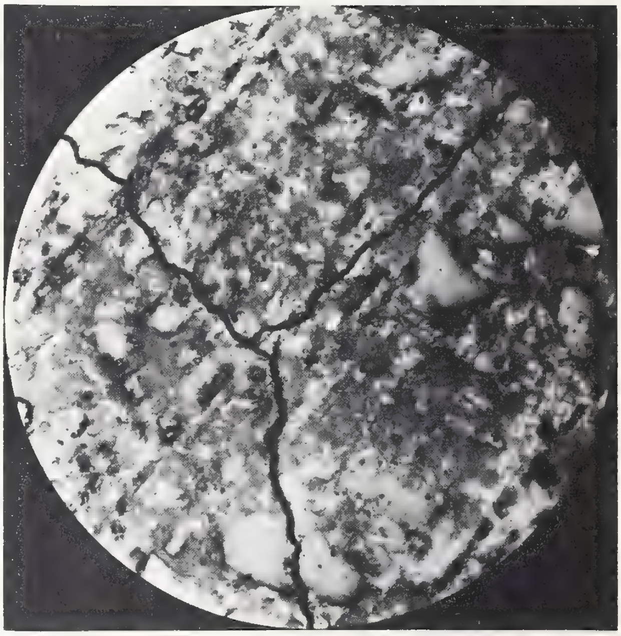

FIGURE 1. *Photomicrograph showing unhydrated cement particles.*

(×220)

It was stated earlier that the nonlinear relationship which has been found between C_3A content and sulfate resistance might be due to errors in estimating the C_3A content and to physical factors such as denseness and permeability of the hardened cement product; a further possibility is that the nonlinear relationship might be due to the existence of different forms of hydrated aluminates. When anhydrous aluminates react with water, metastable equilibrium conditions prevail and platelike metastable aluminate hydrates are formed. On prolonged storage under appropriate conditions, the metastable compounds alter to stable materials. It is conceivable that the metastable and the stable compounds will react differently in an aggressive environment. Numerous investigators have studied the system Al_2O_3–CaO–H_2O either at room temperature or at elevated temperatures and have shown that different hydrated aluminates are formed, depending on the conditions of the experiments.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Other investigators, notably Malquori and Cirilli [11] and Jones [12] have worked on the system $3CaO{\cdot}Fe_2O_3{-}H_2O$ and have produced evidence that hydrated compounds similar to the hydrated calcium aluminates are formed. In the system $4CaO{\cdot}Al_2O_3{\cdot}FeO_3{-}H_2O$ solid solutions of aluminate hydrates and ferrite hydrates are produced.

The reaction of the hydrated cement compounds with various chemical media is of considerable importance with respect to corrosion of hydraulic cement, but, since many of the compounds are metastable, and their formation depends on the conditions of hydration, it is difficult to predict with absolute certainty the behavior of a cement of known composition for different conditions of use.

Corrosion in Sulfate Solutions

The action of sulfates on cement compounds is dependent not only on the compound composition but also on the type of sulfate [13]. Furthermore, it should be realized that the speed of reaction and, in many instances, the nature of the reactions, are modified by the physical state of the cement product.

Practical experience has shown that the resistance of cement products to sulfates is dependent in no small measure on the cement content, the density, and the permeability of the product. Figure 2, for instance, illustrates how an asbestos cement pipe made with an ordinary portland cement with an average C_3A content, has withstood the action of sulfates; a layer of calcium sulfate half an inch thick has built up inside the pipe over a number of years. Except for a few circumferential cracks the pipe was still in good condition.

Ever since it was first observed that hardened portland cement was vulnerable to attack by sulfates, the system $CaO{-}Al_2O_3{-}CaSO_4{-}H_2O$ has been extensively investigated. It was shown by early workers that the calcium sulfoaluminate which is responsible for the deterioration of hardened portland cement in sulfate solutions is identical to the naturally occurring mineral ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). A low-sulfate form was prepared and identified by Lerch, Ashton, and Bogue [14]. Subsequently, Jones [12] has studied the system and has shown that a solid solution series involving $C_3A{\cdot}3CaSO_4{\cdot}32H_2O{—}C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O{—}C_3A{\cdot}CaSO_4{\cdot}12H_2O$ exists. More recently, J. D'Ans and H. Eick [15] have shown the existence of mixed crystals of $C_3A{\cdot}CaSO_4{\cdot}12H_2O$ and $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ in the system $CaO{-}Al_2O_3{-}CaSO_4{-}H_2O$.

This information shows that, although the alumina content of a cement is of considerable importance, the state of equilibrium after hardening with respect to the hydrated aluminates, and especially with respect to $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, will influence vulnerability to sulfate ions. Hydrated supersulfated slag cements are rich in $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ and are stable in the presence of sulfate ions. On the other hand, it has been shown that the cations in the solution have a marked influence on the nature and speed of reaction during attack by sulfates, and in this connection van Aardt [16] has shown that it is incorrect to say that supersulfated slag cements are resistant to sulfates; it should rather be stated that they are resistant to attack by the sulfate ion.

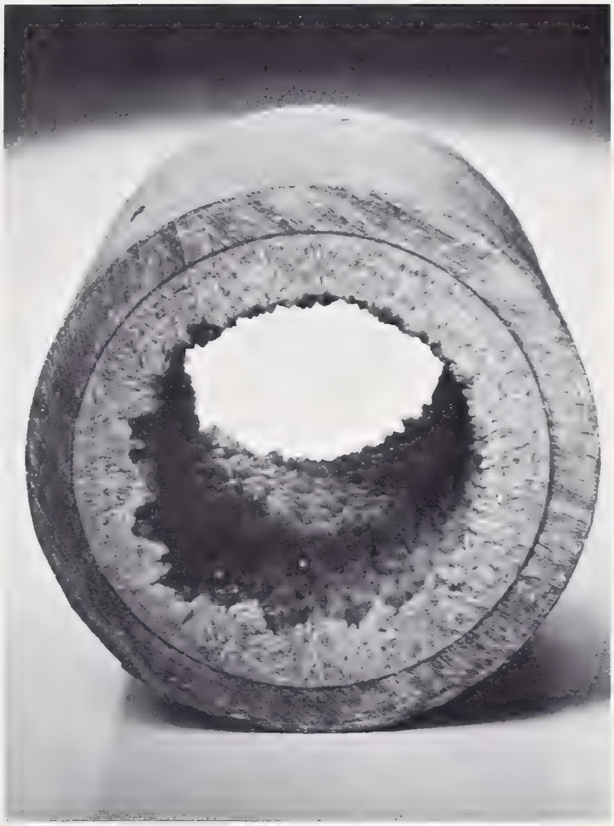

FIGURE 2. *Crystalline calcium sulfate deposit in an asbestos cement pipe.*

Figures 3A and 3B illustrate the behavior of a supersulfated slag cement mortar in sodium, magnesium, and ammonium sulfates, while figure 3C shows the severe attack by magnesium sulfate. The data presented in this figure, and the further experimental data given in subsequent sections of this paper, were obtained by methods and procedures as described by van Aardt [17].

Similarly, extensive work on portland cement, carried out at the National Building Research Institute and elsewhere, has indicated how incorrect it is merely to speak of sulfate resistance or sulfate attack without qualifying the statement by mentioning the cations involved. It has been found that all cements of the portland type so far examined are corroded by magnesium sulfate, and in many cases it is not a sulfate-ion attack but decomposition of the cement by other chemical

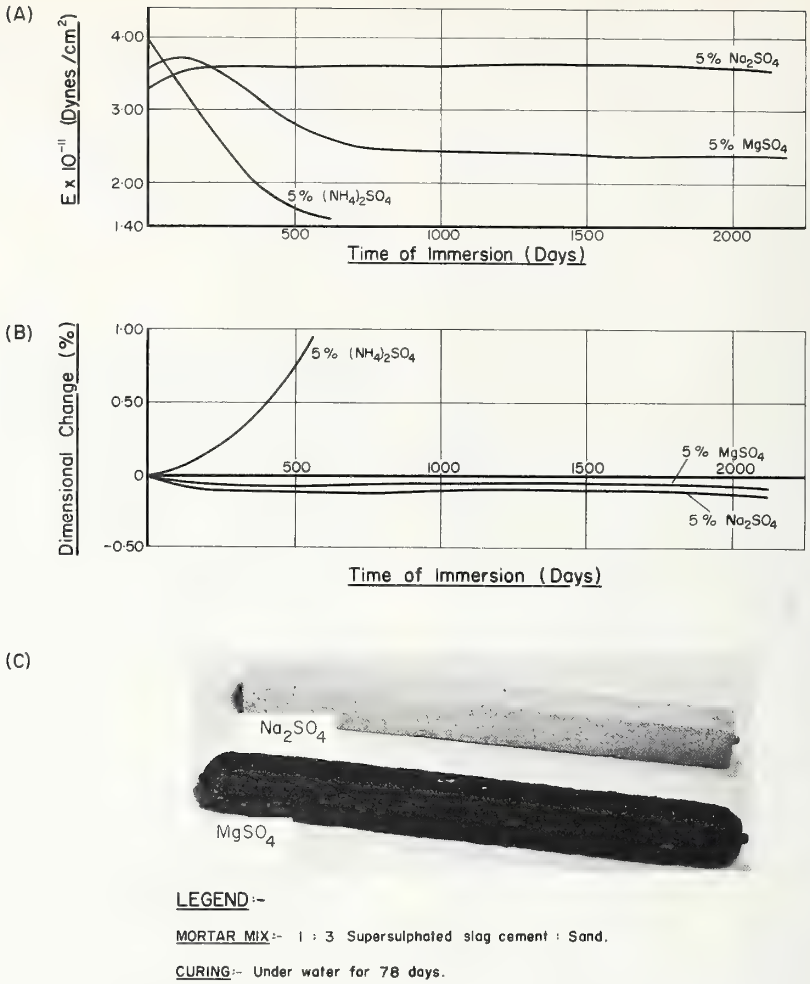

FIGURE 3. *Behavior of supersulfated slag cement mortar in 5 percent sulfate solutions.*

A. Relationship between time of immersion and dynamic modulus of elasticity.
B. Relationship between time of immersion and dimensional change.
C. Specimen showing attack by magnesium sulfate solution.

actions. These cements are in fact chemically stable only in a liquid environment of *p*H above approximately 11.5. At lower values a labile state exists, and reaction with salts such as magnesium sulfate is possible; this salt will react with the hydrated silicates to form magnesium hydroxide and calcium sulfate, while free silica is deposited. A reaction of this nature will decompose the binder.

Van Aardt [16], in studying the behavior of mortar specimens, has found that up to an expansion of about 0.4 percent, the rate of expansion for a particular cement in 5 percent magnesium sulfate solution was approximately constant for all specimens cured under water. The rate of expansion is, however, not constant throughout the entire period during which a specimen is immersed in such a solution.

The initial rate of expansion, i.e., after short immersion periods, can often provide an indication of sulfate vulnerability, since specimens which show rapid expansion are generally more susceptible to an aggressive environment than specimens which show a slow rate of expansion. Even though the ultimate expansion of the latter may be considerable this expansion does not seem to affect the quality of the material adversely. To demonstrate this fact, use has been made of the following method of measuring quality of mortar specimens. If, when a specimen deteriorates, there is only slight variation in dimensions, the natural transverse frequency of vibration is directly proportional to the dynamic modulus of elasticity, i.e., the quality of the material; the drop in frequency is, therefore, a measure of deterioration. Figure 4 illustrates that specimens which show considerable expansion can still be of high quality if the expansion has taken place slowly. It is suggested that this is due to the fact that the material can take up slow expansion, possibly by creep, without disruption taking place. With a slow rate of expansion there may also be some autogenous healing of cracks. However,

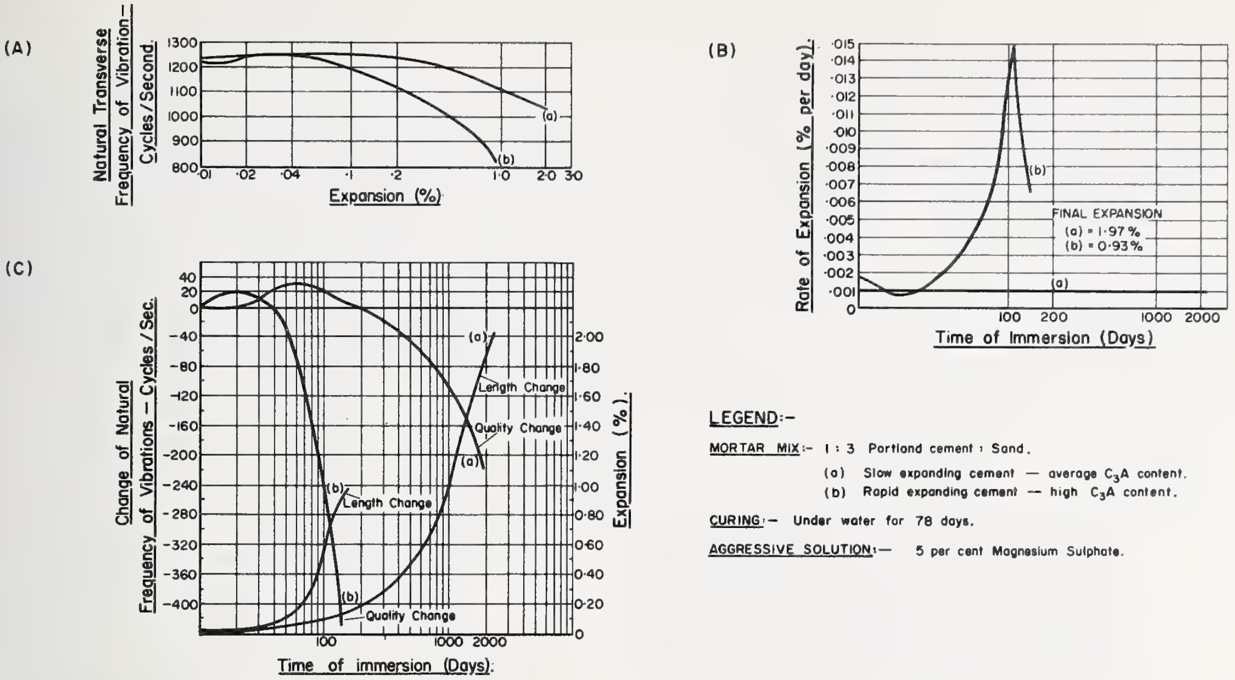

Figure 4. *Behavior of specimens in 5 percent magnesium sulfate solutions.*

A. Relationship between natural transverse frequency of vibration and expansion.
B. Relationship between rate of expansion and time of immersion.
C. Relationship between quality change, length change, and time of immersion.

disruption occurs if substances are present which can yield $CaSO_4{\cdot}2H_2O$ and $C_3A{\cdot}CaSO_4{\cdot}32H_2O$ at a rapid rate. The deterioration by chemical decomposition of the cement compounds in the interior of a dense mortar or concrete, for instance, under mildly acid conditions, is apparently a slow process compared with the disruptive action due to the formation of $CaSO_4{\cdot}2H_2O$ and $C_3A{\cdot}CaSO_4{\cdot}32H_2O$. Specimens in magnesium sulfate clearly deteriorate by the action of two distinct processes, namely by expansion and subsequent disruption, and by destruction of the silicate hydrates due to chemical action. The second process causes a disintegration which first becomes evident by the crumbling of the edges and surface layers, extending to greater depths over longer exposure periods.

The nature of the action of sodium sulfate on portland-cement products is sometimes unpredictable. If a small permeable region in a good quality specimen allows the penetration of sodium sulfate, local expansion, disruption, and subsequent cracking can destroy the mortar, in the fashion apparent from figure 5(a). Figure 5(b) shows a well-compacted portion of the same specimen.

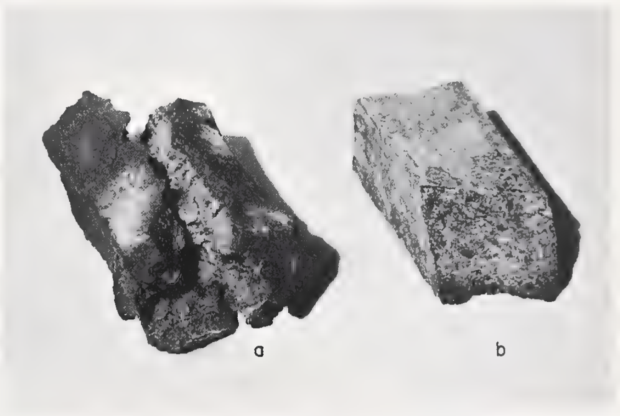

Figure 5. (a) (Left) *Expansion and disruption occurring in 5 percent sodium sulfate.* (b) (Right) *Well-compacted portion is practically unaffected.*

With high-alumina cement it was found that the corrosion resistance to sulfate ions is dependent on the state of equilibrium reached during hydration; the metastable aluminates are more resistant to sulfate attack than are the stable compounds. It is, however, not clear why the stable form of calcium aluminate hydrate, namely tricalcium aluminate hexahyhrate ($C_3A{\cdot}6H_2O$) should be more vulnerable in this instance than the metastable hydrated aluminates, while with portland cements it was found that when stable conditions are reached, for instance by autoclaving, the cement product is more resistant to sulfate ions.

As with other hydraulic cements, corrosion of high-alumina cement by sulfates depends on the type of sulfate involved, but the relative vulnerability in some cases is changed as compared to the other cements, e.g., high-alumina cement is more resistant to ammonium sulfate and magnesium sulfate than are the other cements. In 5 percent sodium sulfate solution, its behavior is apparently markedly influenced by the nature of the hydrates as determined by the state of equilibrium reached under the conditions of hydration.

The resistance of high-alumina cement to sodium sulfate can be good, but under certain circumstances it may be poor. It is known that hydrated high-alumina cement is vulnerable to caustic alkalies and the formation of sodium hydroxide is possible if high-alumina-cement products are subjected to sodium sulfate solutions. Figures 6A and 6B illustrate the behavior of high-alumina cement mortars in various sulfate solutions. Figure 6C shows the extent of deterioration by sodium sulfate.

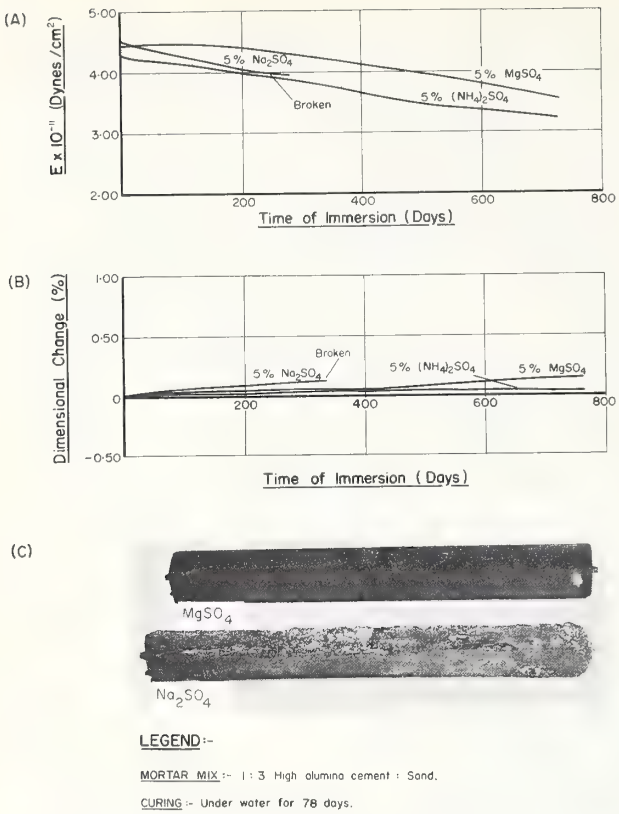

FIGURE 6. *Behavior of high-alumina-cement mortars in sulfate solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Specimens showing attack by sodium and magnesium sulfate solutions after 650 days.

Corrosion in Chloride Solutions

In chloride solutions, as with sulfates, the cations of the aggressive medium have a significant effect on the corrosion of cement products.

Figures 7 and 8 show the behavior of 1:3 cement-mortar specimens, made with various hydraulic cements, in 5 percent solutions of sulfates and chlorides. Over the periods of these tests, magnesium chloride seems to have very little effect on high-alumina cement; there is a slow expansion but no deterioration in quality. The portland-cement specimens showed a marked initial drop in quality, whereas the supersulfated slag cement showed an initial drop and a subsequent increase to a constant value of quality, while the sulfate-resisting cement showed no change in quality. The cements showed a slow expansion in magnesium chloride solutions; the largest expansion was observed for the portland cement, followed by the sulfate-resisting portland cement.

In 5 percent sodium chloride, high-alumina-cement specimens showed a marked initial drop in quality and a slow surface disintegration. The quality of the other cements remained fairly constant during the time of exposure. Especially for the portland cement and the high-alumina cement, however, there was expansion. In ammonium chloride there was a similar drop in quality for specimens made with the various cements, and the specimens showed slight shrinkage, the largest shrinkage being observed for the sulfate-resisting portland cements.

Corrosion in Mixtures of Sulfates and Chlorides

It has previously been suggested [16, 18] that chloride ions might have the effect of decreasing attack on portland cement products by sulfates, but it now appears that this effect is insignificant and that sulfate expansion and deterioration proceed in the presence of large amounts of chloride ions. The data presented in figures 7 and 8 seem to verify this last observation although there was a slight reduction in length change, but this can be attributed to the lower sulfate concentration, as chloride ions were substituted for some of the sulfate ions in these experiments.

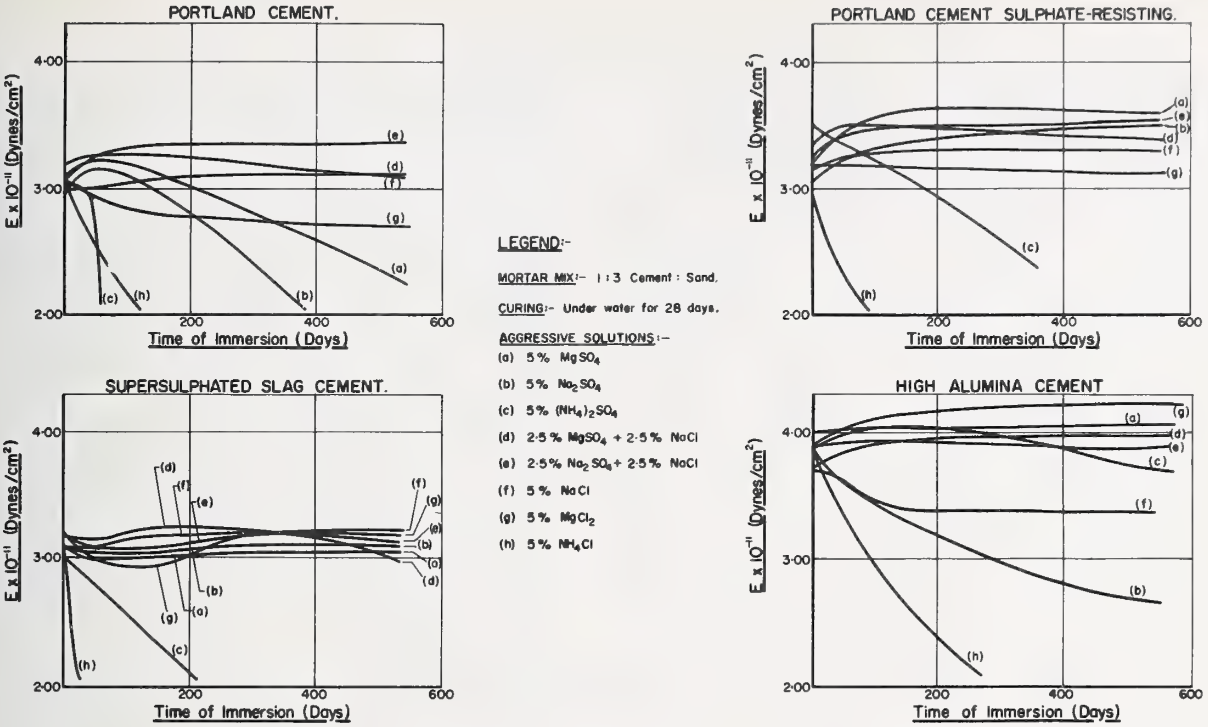

FIGURE 7. *Behavior of various cement mortars in aggressive solutions.*

Relationship between dynamic modulus of elasticity and time of immersion.

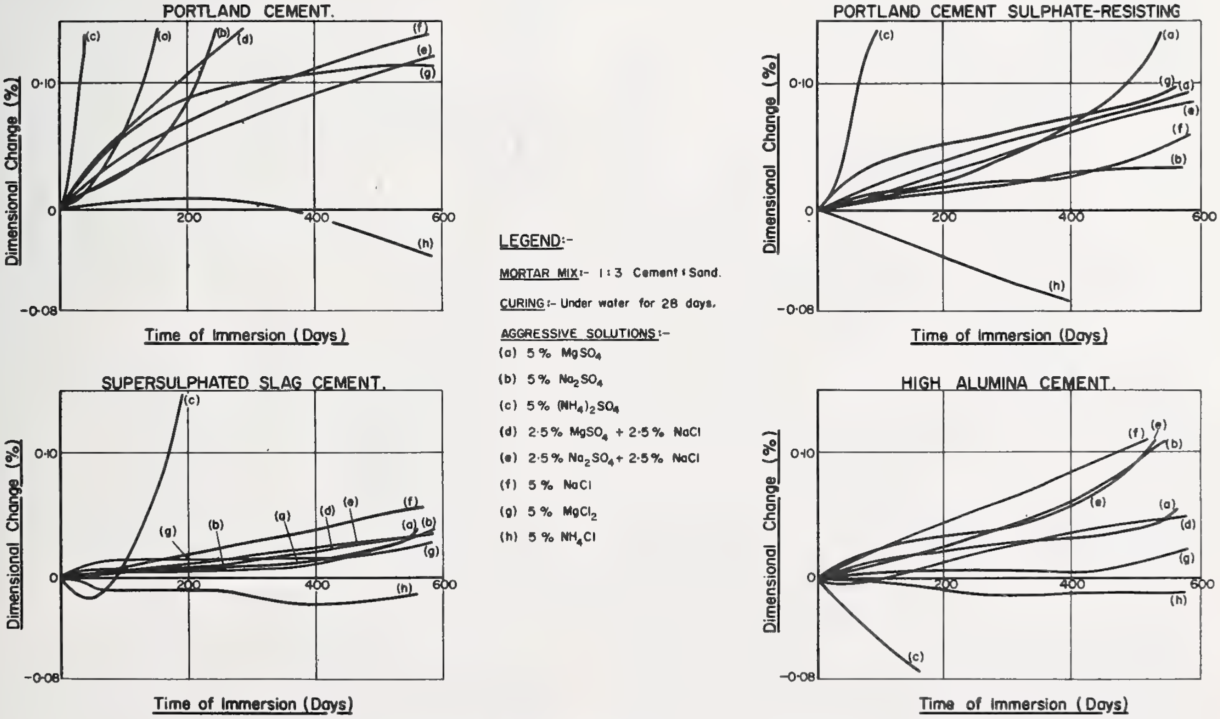

FIGURE 8. *Behavior of various cement mortars in aggressive solutions.*

Relationship between dimensional change and time of immersion.

Corrosion by Acids

Since hydraulic cements are basic materials, it can be expected that they will be vulnerable to strong and even weak inorganic and organic acids. It is, however, interesting to study the nature and speed of attack of various acids on such cements and, furthermore, such a study has furnished useful information, since cement products are in fact often subjected to acid environments. Due to the basicity of hydraulic cements, acids cannot penetrate dense mortars or concrete without destroying the material as they they travel inwards into the material, while at the same time the acids are neutralized. Thus, unless the product is very open-textured, purely acid destruction takes place from the surface inwards and this type of corrosion is more markedly influenced by concentration of the aggressive media than in the case of salt attack. If the acid is of a type containing an anion which attacks cements, the anion penetrates the product and causes destruction ahead of the acid front. It is thus apparent that some acids have a twofold attack on cement products, namely the purely acid attack and the salt attack.

Figure 9 illustrates the behavior of portland-cement mortars in various acid solutions. The data show that neither dimensional change alone nor weight loss alone is always a true measure of deterioration. Furthermore, it is not uncommon for a cement product to be destroyed by salt action before any significant portion of the cement is neutralized and destroyed by the acid attack. This destruction often takes place in low acid concentrations, while in high acid concentration the acid attack is predominant, and the specimen is destroyed before any marked salt action can occur.

This relative acid-salt attack is conveniently illustrated by immersing normal portland cement mortars in 1 and 5 percent sulfuric acid solutions. It is found that most of the damage is done by sulfate attack in the 1 percent acid, while the acid attack is mainly responsible for the destruction in the 5 percent acid solutions.

These considerations are of significant practical value and explain many of the observations made when various hydraulic cements are in contract with acid solutions. In fact there is generally very little difference in the resistance of various hydraulic cements to acids only, and the fact that some of these perform better than others in particular acids, depends on whether or not secondary reactions occur.

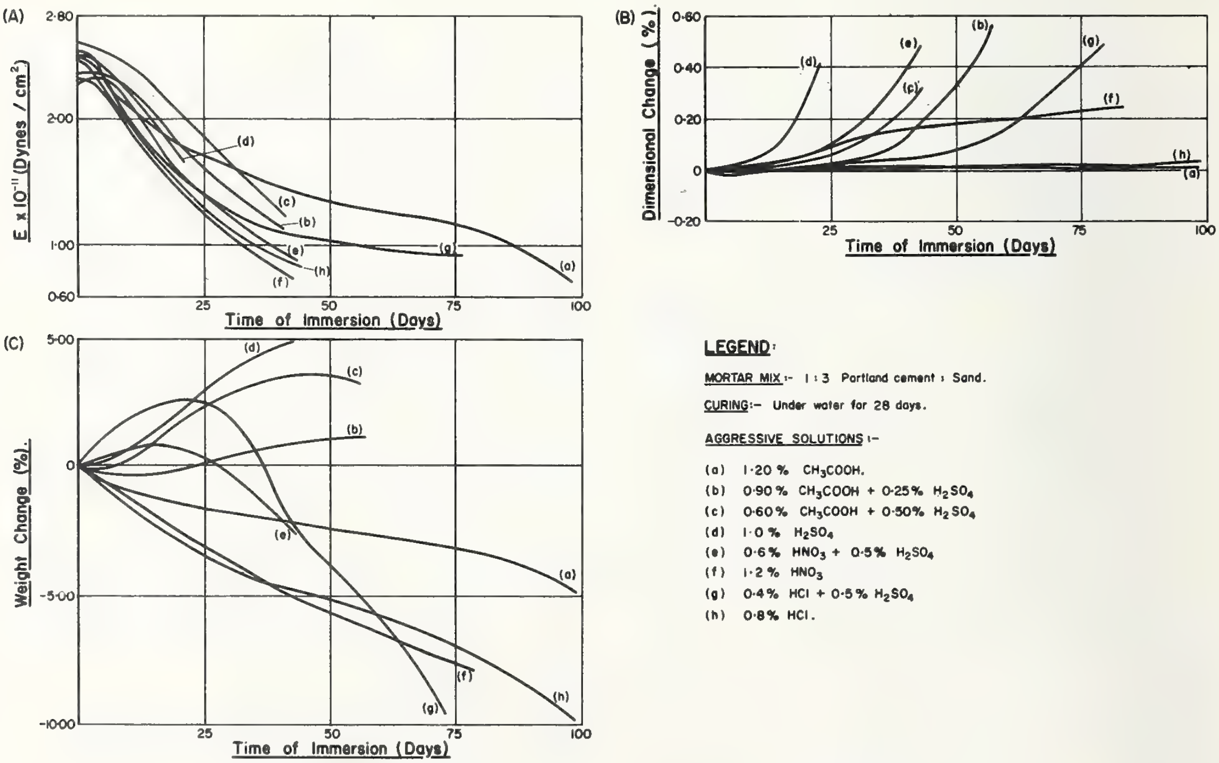

FIGURE 9. *Behavior of portland cement mortars in various solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Relationship between weight change and time of immersion.

Deterioration of Cement Products in Soft and Pure Waters

Since hydrated cement compounds are slightly soluble in water, it follows that they will be slowly removed from a cement product by solution. Furthermore, the hydrated compounds are, in general, incongruently soluble in water and certain components of the hydrated cement will be removed preferentially. Since hydrated silicates are unstable in contact with water having a low *p*H, slight decomposition takes place until the calcium hydroxide content of the liquid in contact with the silicate is at the equilibrium level. If this liquid is replaced by fresh water, more decomposition will take place, and, if the process is repeated over a long period, this leaching of calcium hydroxide will result in complete decomposition of the hydrated calcium silicates. Only insignificantly small quantities of lime will be removed in this way if the water is hard, but incrustation might occur. In moderately hard water the action is negligible.

Soft water, however, is aggressive, the agressiveness being a function of the calcium carbonate, calcium bicarbonate, and carbon dioxide contents and of the *p*H of the water. The rate of dissolution in soft water is high if the aggressive carbon dioxide content is high. The aggressive carbon dioxide is that portion of the free carbon dioxide in excess of the quantity required for the stabilization of the carbonate-bicarbonate equilibrium.

$$CaCO_3+H_2CO_3\rightleftharpoons Ca(HCO_3)_2$$

The higher the concentration of calcium bicarbonate, the higher will be the quantity of free carbon dioxide required for stabilizing the equilibrium, and hence, for the same amount of free carbon dioxide, the lower will be the amount of aggressive carbon dioxide.

Reaction of Inorganic and Organic Anions and Acid Radicals With Hydraulic Cement Minerals

Since cement is often used in contact with various organic and inorganic acids and since these substances combine with the calcium and aluminum ions in the cement to form calcium-aluminum hydroxy-salts, a thorough understanding of their characteristics is essential. Their significance in the field of cement chemistry has long been realized; they have an influence on the setting and hardening of cement and on the durability and resistance of cement products to attack. Some characteristics are probably significant in regard to the corrosion of steel in concrete. Much has already been said about the two sulfate double salts of calcium-aluminum, namely $C_3A\cdot 3CaSO_4\cdot 31H_2O$ and $C_3A\cdot CaSO_4\cdot 12H_2O$, but many others, such as chloride, carbonate, nitrate, are known.

Savvina and Serb-Serbina [19] have shown how the calcium-aluminum hydroxy-chlorides have an influence on the durability of hardened cement in concrete. Feitknecht and Buser [20] have distinguished and described two types of calcium-aluminum hydroxy-salts, namely needle-shaped and plate-shaped materials. Little work has been done on calcium-aluminum hydroxy-salts involving an organic radical. A plate-shaped picrate was described by Feitknecht and Buser [21].

Using the method of preparation described by Feitknecht and Buser, a number of double salts containing inorganic and organic anions were prepared and examined. Plate-shaped nitrite and sulfite crystals similar to the chloride and nitrate were obtained.

The work was extended to benzoates, including substituted benzoates. All these gave plate-shaped crystals except *p*-nitrobenzoate which gave needle-shaped crystals. X-ray diffraction diagrams of the various salts are given in figure 10.

The calcium-aluminum hydroxy *p*-nitro-benzoate crystals are similar in shape and appearance to ettringite. Calcium-aluminum hydroxy *p*-nitrobenzoate was also prepared by mixing calcium *p*-nitrobenzoate with C_3A, $C_3A\cdot 6\ H_2O$, portland cement, or high-alumina cement. Needle-shaped crystals, as shown in figure 11, and similar to those of ettringite, were obtained.

The Influence of Curing Conditions on the Behavior of Cement Products in Aggressive Media

The importance of thorough curing in obtaining cement products which are resistant to attack has been realized and demonstrated, yet in practice full advantage of thorough curing is not always taken. It is often assumed that the mixing water is sufficient to achieve this; in practice, however, especially in arid and hot climates, loss of moisture due to evaporation and, in plasters and mortars, due to absorption by the materials on which they are used, can lead to inadequate curing.

Furthermore, the curing procedure per se has a marked influence on the resistance of cement products to aggressive agents.

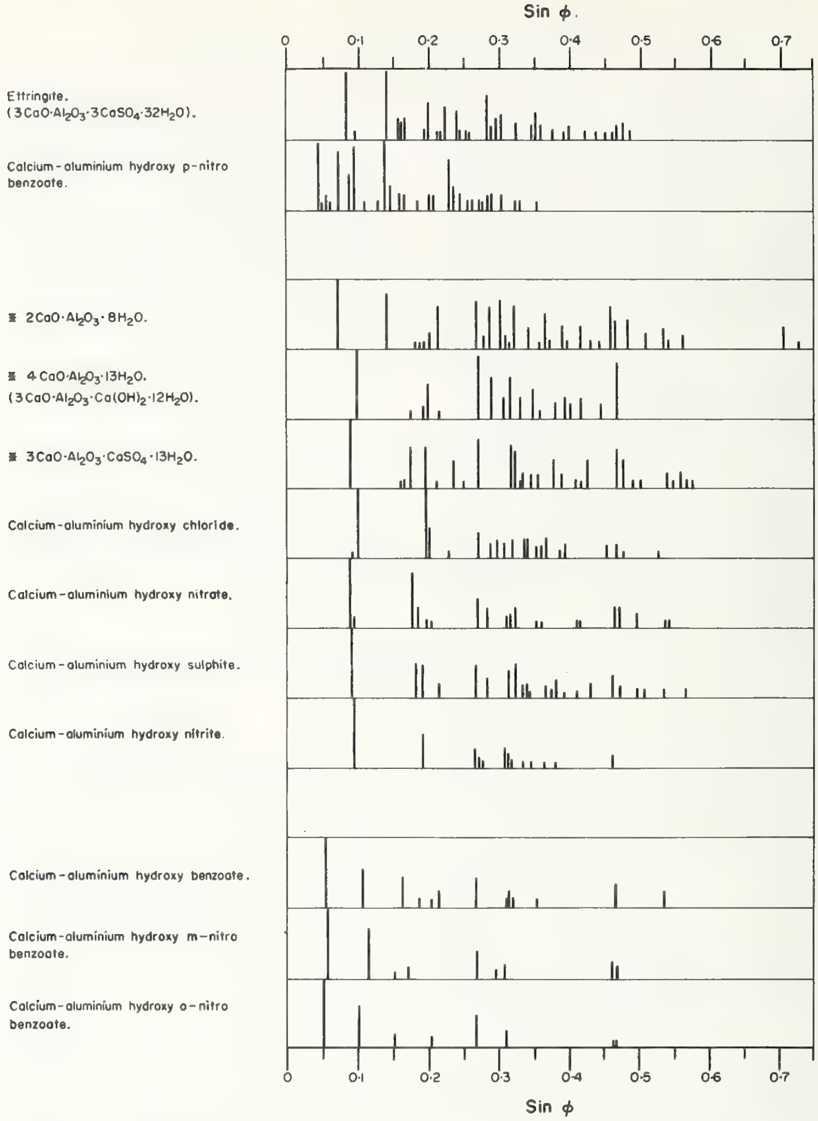

FIGURE 10. *X-ray diffraction diagrams of various calcium-aluminum hydroxy-salts.*

(Radiation—Copper $K_{\alpha 1}$; $\lambda = 1.54050$A).

* Zement-Kalk-Gips No. 12, p. 517, table 2 (1957).

Steam Curing

High-Pressure Steam Curing

Steam curing and, in particular, high-pressure steam curing has an advantageous effect on the resistance of mortars and concrete to sulfate solutions. This improvement is largely attributable to the formation of more stable, low-lime hydrates and also to reaction between silica and lime, which decreases the amount of free lime in the hardened product and thus reduces vulnerability. The formation of silica-alumina-lime complexes is also advantageous. It can be demonstrated, however, that although the resistance of steam-cured products to, for instance, sodium sulfate, is vastly increased, such products are still vulnerable to magnesium sulfate, as shown in figure 12. In figure 13 it is apparent that the substitution of a dolomitic calcareous aggregate for a siliceous aggregate in similar high-pressure, steam-cured mortars, made with the same cement, did not reduce resistance to magnesium sulfate but rather increased it. This observation seems to indicate that the lime-silica reaction is not the major factor contributing to the greater resistance of autoclaved specimens to this sulfate.

Low-Pressure Steam Curing

It was found that steam curing under atmospheric pressure did not have a significant influence on the behavior of cement products in aggressive solutions when compared with similar products cured in a humid atmosphere.

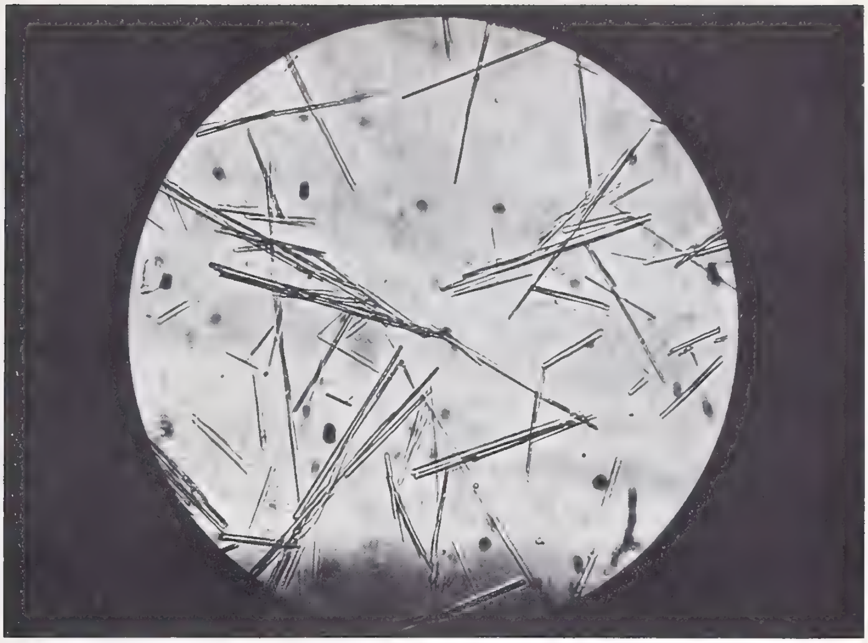

FIGURE 11. *Photomicrograph showing crystals of calcium-aluminum hydroxy p-nitro-benzoate.* (×395).

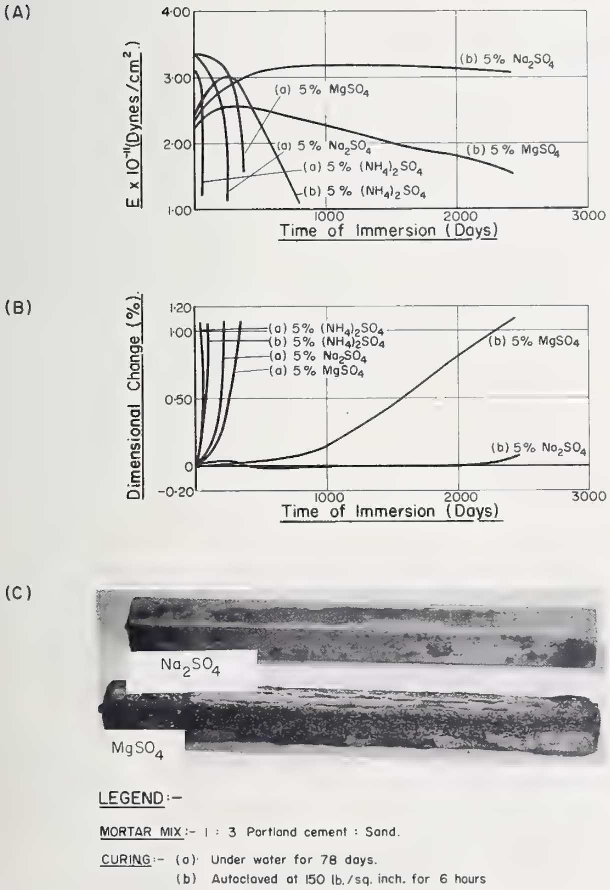

FIGURE 12. *Behavior of autoclaved and water-cured portland-cement mortars in sulfate solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Autoclaved specimens showing attack by 5 percent sodium and magnesium sulfate solutions after 7 yr.

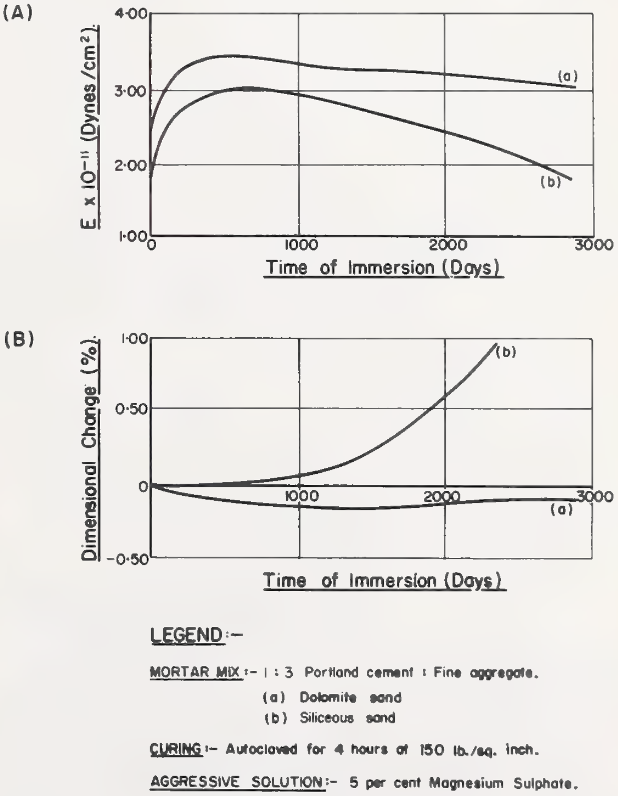

FIGURE 13. *Behavior of autoclaved cement mortars containing dolomitic and siliceous sand in 5 percent magnesium sulfate solution.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.

Underwater Curing and Humid-Atmosphere Curing

Van Aardt [17] has shown that mortar specimens cured under water, prior to immersion in sulfate solutions, were more vulnerable than specimens cured in an atmosphere of 80 percent rh. For specimens cured in saturated air the resistance to sulfates was less than for those cured in the 80 percent rh environment, since in saturated air, underwater conditions are approached. Figure 14 illustrates the behavior of two portland-cement mortars, cured under different conditions, when immersed in a 5 percent solution of magnesium sulfate.

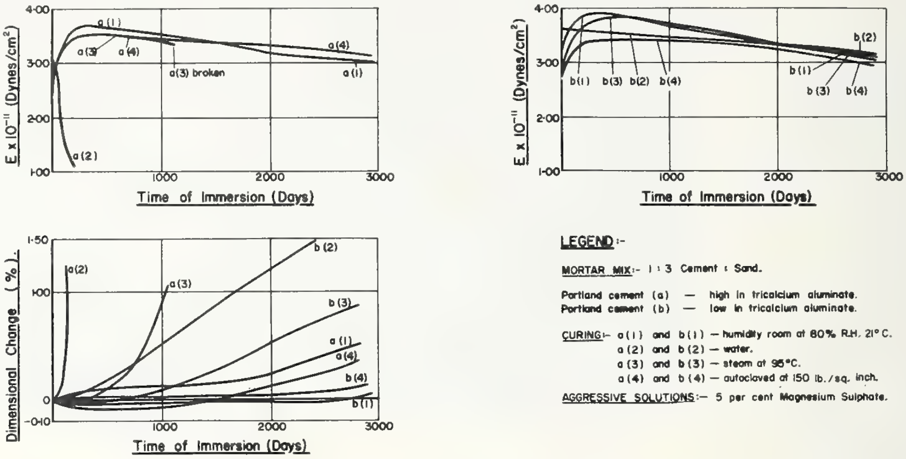

FIGURE 14. *Dynamic modulus of elasticity and dimensional changes of two portland cement mortars cured under different conditions.*

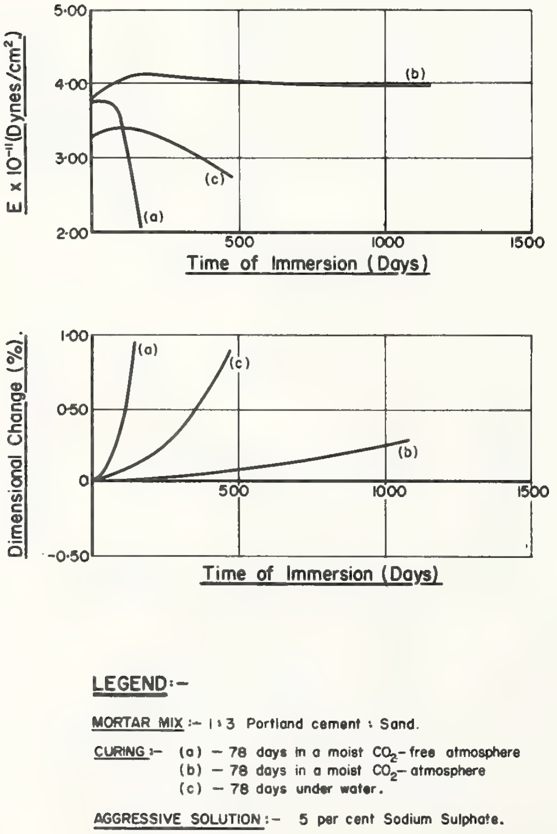

FIGURE 15. *The effect of carbonation on the resistance of portland cement mortars in 5 percent sodium sulfate solutions.*

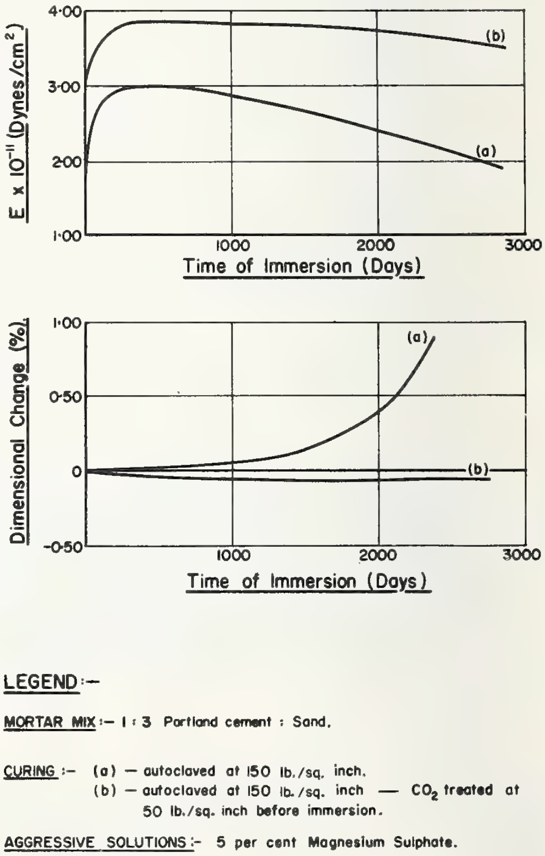

FIGURE 16. *The effect of carbonation on the resistance of autoclaved portland cement mortars in 5 percent magnesium sulfate solutions.*

Carbonation of Cement Products During and After Curing

Leber and Blakey [22] have determined the effect of gaseous carbon dioxide on the strength and shrinkage of mortars and concretes. They found that strength is increased and shrinkage decreased if specimens undergo a period of curing in carbon dioxide immediately after demolding. Results obtained by Verbeck [23] showed that carbonation of hydrated portland-cement pastes had advantageous effects on the products with regard to strength, hardness, permeability, and volume stability.

Carbonation of hydrated portland-cement products also improves their behavior in aggressive media. Portland-cement mortar specimens cured in a carbon dioxide-free environment have poor resistance compared to carbonated or partially carbonated specimens. This observation is illustrated in figures 15 and 16. In contrast to the above, early carbonation has an adverse effect on the quality of supersulfated slag cement products, and carbon dioxide should be excluded during the early curing period when these cements are used.

The Influence of the Nature and Type of Aggregate on Corrosion Resistance

The important finding that the substitution of a calcareous aggregate, such as good quality limestone or dolomite, for a siliceous or other noncalcareous aggregate has a very significant beneficial effect on the corrosion of cement products in certain aggressive media, has been extensively studied. In acid solutions the useful life of the product can be extended appreciably by the use of calcareous aggregate; this can be seen from figure 17. It appears that not only does the acid-soluble aggregate "protect" the cement in that it aids in neutralizing the acid, but it also has a retarding effect on the expansion resulting from sulfate attack in acid solutions; the carbon dioxide produced when the acid reacts with the carbonate aggregate apparently reduces the formation of tricalcium sulfoaluminate.

If portland-cement products made with a nonsiliceous aggregate are autoclaved, the materials produced generally have lower strength than those made with siliceous aggregates, but research has shown that they have good resistance to sulfuric acid and sulfates.

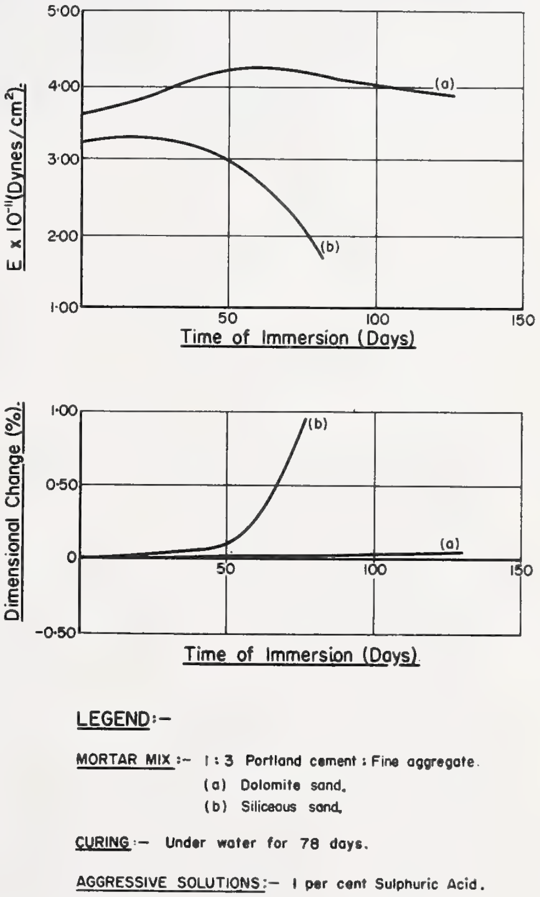

FIGURE 17. *Comparison of the behavior in 1 percent sulfuric acid solution of portland cement mortars made with dolomitic and siliceous sand.*

General Remarks on Corrosion Studies

Studies aimed at evaluating the corrosion resistance of hydraulic cement products are difficult owing to the complexity of the problem; it is not sufficient to determine the chemical reactivity of the unhydrated neat cements or hydrated neat cements, because they are in practice not subjected to aggressive environments in these states. Therefore the accelerated tests of the kind described in this paper can serve only as a guide and should be considered as such.

An attempt was made to evaluate cements in a state in which they are used, but since cement products are so variable with respect to quality, even when made under strictly controlled conditions, it is practically impossible to produce in the laboratory products which are in all respects comparable with those made in actual practice, and hence statistical correlation, between laboratory results and long-term practical exposure and use, is essential. Furthermore, it is difficult to simulate in the laboratory the varied conditions of exposure found in practice.

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Discussion

T. D. Robson

When testing high-alumina cement mortars or concretes in sulfates or salt solutions there are one or two points which may need attention if apparently contradictory results from different workers are to be avoided.

As the author has said, the resistance of specimens containing the normal hexagonal calcium aluminate hydrates may be different from that of specimens kept in conditions where substantial conversion to the stable cubic hydrate can occur. The resistance properties obtained from each of the two types of hydrate should therefore, in our opinion, be first examined separately. Accordingly, if the normal resistance properties of high-alumina cement are to be tested in this way, there is much to be said for making and storing the specimens at a controlled low temperature (say, below 70 °F) so that any possible effect of conversion can be eliminated from initial consideration.

For example, tests carried out at an unspecified temperature range, at "room temperature" or "in the laboratory," may cause confusion between investigators in different parts of the world, since local temperature conditions may be sufficient, in some cases, to cause appreciable conversion to cubic hydrate within the test period. The effect of total conversion of hydrates on the sulfate resistance of high-alumina cement can best be determined as a separate operation by keeping the specimens in test solutions maintained at over 85 °F or by fully converting the hexagonal hydrates, by heat treatment, before placing the specimens in the solutions.

When this is done, it has been found that the properties of the "fully converted" high-alumina cement specimens (including the chemical resistance properties) are chiefly dependent on the water-cement ratio used [1, 2]. Roughly speaking, specimens made with a water-cement ratio below 0.4 still show high chemical resistance even if all the hydrate is converted to the cubic type, but those made with much higher water-cement ratios usually give reduced resistance if kept in conditions where appreciable conversion takes place.

In brief, specimens made with either high or low water-cement ratios give excellent chemical resistance if one is dealing with the normal hexagonal hydrates, but the resistance obtained under conditions causing conversion is largely dependent on the water-cement ratios.

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Discussion

L. R. Blair and Julie Chi-Sun Yang

In the paper of J. H. P. van Aardt entitled "Deterioration of Cement Products in Aggressive Media," much has been said concerning the chemical stability of cement and cement products. Our laboratory has devoted much effort to a study of the chemical stability, particularly in sulfate media, of asbestos-cement products, and the results of these investigations are summarized below.

Prior to beginning a discussion on the chemical stability of asbestos-cement materials, it is necessary to emphasize the fact that these products may be cured by one of two different procedures. The type of curing has been found to exert a strong influence on product stability in various chemical environments. The first of these is termed "normal" curing, which is generally conducted at atmospheric pressure either under water or in a moist atmosphere for periods of time usually in excess of 28 days. The second type of curing is accomplished by first storing in a moist atmosphere for 24 hr and then treating in an autoclave operated at pressures between 100 and 200 psi under saturated steam conditions for periods of 16 hr or more.

The starting formulations as well as the final chemical assembly of asbestos-cement products vary with the curing conditions. If a product is to be normal-cured, its starting dry formulation usually contains approximately 20 percent of a fiber blend and 80 percent of portland cement, normally of the Type I variety. Autoclave-cured formulations, on the other hand, contain approximately 20 percent of the fiber blend and 80 percent of a quartz flour-portland cement mixture in a ratio of 0.6 quartz to 1.0 portland cement. There is a vast difference between the chemical stability of normal and autoclaved asbestos-cement products, the autoclaved products being generally superior. In addition to laboratory test results, field results also emphasize this point. Two field experiences will be discussed briefly to illustrate this conclusion.

In the first instance a normal-cured asbestos-cement pipeline was installed by the town of Ordway, located in southeastern Colorado. This line was installed in 1934 in a high sulfate-containing soil. Approximately 6 yr later the walls of the pipe eroded in spots, causing leaks and ruptures in the line. A stretch of this line, which was peculiarly situated in relation to pumps and stand towers, was subjected to alternate wetting and drying from the inside. This portion was particularly troublesome, although occasional breaks in other portions of the line also occurred. A portion of the disintegrated pipe removed from service is shown in figure 1. Approximately 13 yr after original installation, the damaged line was replaced with autoclave-cured asbestos-cement products. The new line was located approximately 1½ ft from the old line and ran in a parallel direction. The autoclave-cured material has been in continuous service since that time under conditions duplicating those which cause deterioration in the normal-cured pipe. Recent inspection (1960) has shown there is no visible evidence of sulfate attack.

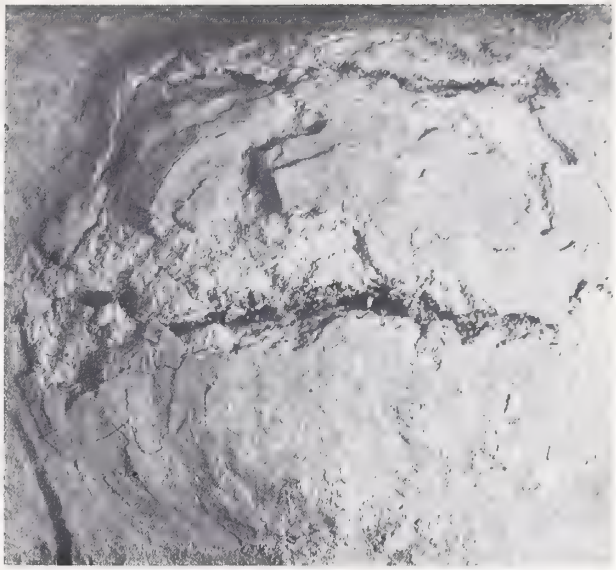

FIGURE 1. *Close-up of corroded normal-cured pipe removed from service at Ordway, Colorado.*

The second long-term field test also illustrates the improved stability of autoclaved products toward a high sulfate chemical environment. In 1931, as part of an extensive program of the study of sulfate attack on cements and concretes [1],[1] Miller also conducted tests on normal-cured asbestos-cement pipe. By 1936 he found that this material did not have ". . . more than normal resistance . . ." to sulfates [2]. Manson [3] stated that these materials were severely attacked in this period of time. At this time autoclave-cured asbestos-cement pipe was introduced to the American market, and Miller decided to test the new products. He and Manson placed 30 sections of the autoclave-cured material under water at Medicine Lake, South Dakota, for tests similar to those used previously on the normal-cured material. The waters of Medicine Lake at that time contained about 12 percent of sulfates, of which two-thirds was magnesium sulfate and one-fourth sodium sulfate.

The crate in which these pipes were submerged became separated from the main body of crates and was lost. It remained at the bottom of the lake until early in 1960, when it was accidentally located and returned to the University of Minnesota for observation and test. After 24 yr in this severe environment, these pipes appear to be physically sound and free from defect.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Although field experience is of necessity limited to attack by sodium and magnesium sulfate solutions, laboratory tests also indicate that autoclave curing increases resistance to attack by other sulfate media, and also by bicarbonate solutions and distilled water.

There are many factors which are thought to contribute to the superior stability of autoclave-cured portland cement products. These are:

(1) The elimination of free calcium hydoxide;

(2) The formation of a better crystallized calcium silicate hydrate;

(3) The elimination of small amounts of hydrated sulfoaluminates; and

(4) The probable elimination of C_3AH_6 as indicated by the fact that it is not detectable by X-ray analysis.

The first two of these factors will be discussed in detail in this paper. Factor 3 has been well covered in previous investigations [4], and factor 4 will be dealt with in a future publication.

The Elimination of the Free Calcium Hydroxide

It has been found that portland cement hydrates rapidly in saturated steam at 100 psi and above, liberating free hydrated lime. Since silica flour is incorporated in the autoclave formulation, this liberated calcium hydroxide in turn reacts rapidly with the quartz to produce a calcium silicate hydrate of the tobermorite variety. Free hydrated lime is also liberated when a cement product is normally cured. However, because there is no silica in the formulation, the calcium hydroxide remains in the product in the free crystalline form. Incorporating silica in a normal-cured formulation does not help the situation since it does not react in detectable amounts with free lime at these low temperatures. Analyses of various autoclave- and normal-cured products show that the former contain not more than 1/2 percent free lime, whereas the latter commonly contain between 13 and 18 percent.

As early at 1897 Candlot [5] found that cements containing free lime disintegrated in salt solutions. This was followed in 1902 by the work of Deval [6] who found that the presence of free lime in a cement reduced its resistance to attack by sulfate environments. These publications have been followed by the work of numerous investigators who have confirmed the original findings [7]. From these investigations it is apparent that calcium hydroxide content is a prime factor in causing sulfate deterioration. Sulfate attack is usually due to chemical reactions within the cement which produce compounds of a greater volume than those originally present, thus causing an expansion and disruption of the cement bond. Any free hydrated lime which is present will react with the soluble sulfates to produce either calcium sulfate with a resultant 200 percent volume increase or ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32\ H_2O$) with also a 200 percent volume increase. These reactions are illustrated in the following formulas:

$$Ca(OH)_2 + SO_4^{=} + 2\ H_2O \longrightarrow CaSO_4 \cdot 2\ H_2O + 2(OH)^{=}$$

$$1\ \text{volume} \longrightarrow 2.97\ \text{volumes} \qquad (1)$$

$$6\ Ca(OH)_2 + 2\ Al^{3+} + 3\ SO_4^{=} + 26\ H_2O \longrightarrow 3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4 \cdot 32\ H_2O$$

$$1\ \text{volume} \longrightarrow 3.04\ \text{volumes.} \qquad (2)$$

Examinations of the deteriorated portions of the Ordway pipe indicate that reaction 2 took place in this instance. Large amounts of ettringite and traces of calcium carbonate were found by microscopic and X-ray examination in the blistered sections. Gypsum was not detected.

Other data also indicate that the presence of free lime results in the deterioration of asbestos-cement products in distilled water and bicarbonate solutions.

The results of tests made by leaching crushed portions of asbestos-cement pipe which contained 13.0 and 0.03 percent free lime in bicarbonate solutions are presented in figure 2. After 9 days, 64 percent of the total lime had been leached out, compared to 40 percent for the sample containing 0.03 percent free lime.

To test the comparative resistance of the same two products in distilled water, portions of pipe were cut into pieces approximately 2 x 3 x ½ in. These portions were immersed in distilled water and the water was changed every 24 hr to simulate

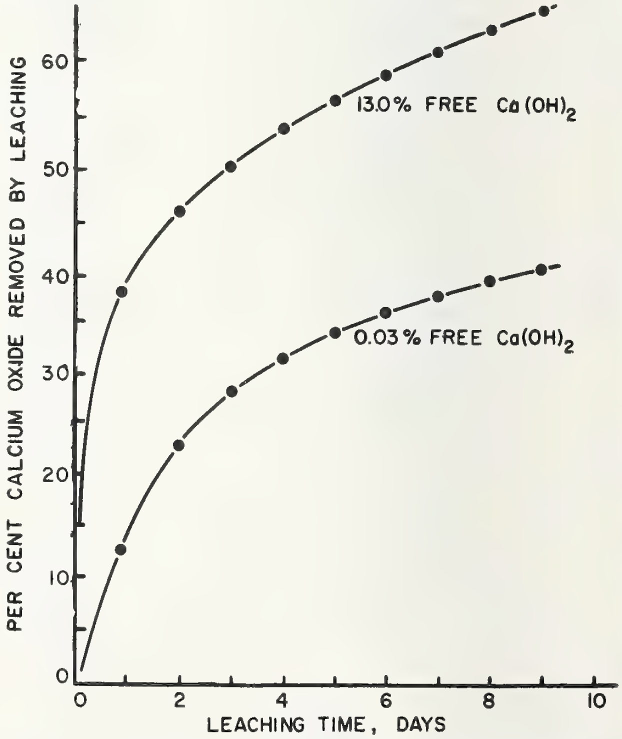


Figure 2. $Ca(OH)_2$ *removed from asbestos-cement samples by continuous leaching of powdered sample with bicarbonate water.*

($NaHCO_3$, 2.2 g/l; NaCl, 2.6 g/l; CO_2 added to bring pH to 6.1) flow conditions in the pipe. The samples were removed from the solution at weekly intervals, dried, and weighed. The weight losses are plotted in figure 3. Here the material containing 13 percent free lime lost approximately 8 percent of its weight at the end of 4 weeks. The material containing 0.03 percent free lime lost but 2 percent.

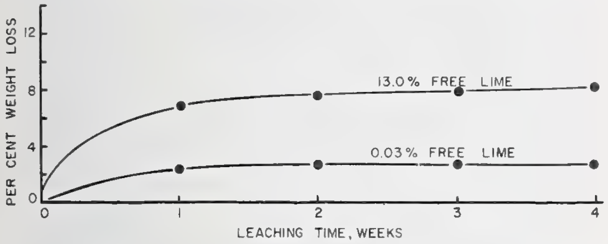


Figure 3. *Resistance of asbestos-cement products to leaching by distilled water.*

The calcium hydroxide contents of autoclave-cured and normal-cured asbestos-cement sag cakes made with Type I and Type V cements and their comparative sulfate resistance, as indicated by U.S. Bureau of Reclamation tests, are shown in table 1. It is interesting to note that normal-cured Type V cement (said to be sulfate resistant) is superior to normal-cured Type I cement. However, when either of these cements is autoclave-cured, differences between the two types are no longer apparent, and the autoclave-cured results are superior to the normal-cured in each instance. Thus, Type V cement does not appear to improve the sulfate resistance of an autoclave-cured product. The chemical analyses of the two types of cement which were studied and their calculated compositions are presented in table 2.

Table 1. *Test data—free lime content and sulfate resistance of normal- and autoclave-cured cements*

Sulfate resistance test, U.S. Bureau of Reclamation

Type of cure	Silica/ cement	Cement type	Free $Ca(OH)_2$	Total expansion after 28 cycles
			%	%
Autoclave, 125 psi, 16 hr	0.6/1.0	I	0.4	0.03
		V	.5	.03
Normal cure, underwater 28 days.	.0/1.0	I	15.5	.16
		V	13.7	.11

Table 2. *Chemical and calculated compound compositions of type I and type V cements investigated*

Constituent	ASTM cement type	
	I	V
	Percent	*Percent*
Ignition loss, 1,800 °F	3.8	1.6
SiO_2	19.5	22.3
Fe_2O_3	2.9	5.5
Al_2O_3	5.9	3.1
TiO_2	.2	.2
P_2O_5	.3	.1
CaO	61.0	62.0
MgO	2.2	2.1
Na_2O	.5	.2
K_2O	.8	.5
SO_3	2.7	2.2
Tricalcium silicate	49.0	48.0
Dicalcium silicate	19.0	28.0
Tricalcium aluminate	11.0	0
Tetracalcium aluminoferrite	9.0	17.0

The limit of calcium hydroxide which may be tolerated in a product subjected to sulfate conditions is difficult to specify. However, it is apparent that any amount of free hydrated lime is detrimental, and therefore the limit should be set as close to zero as practical.

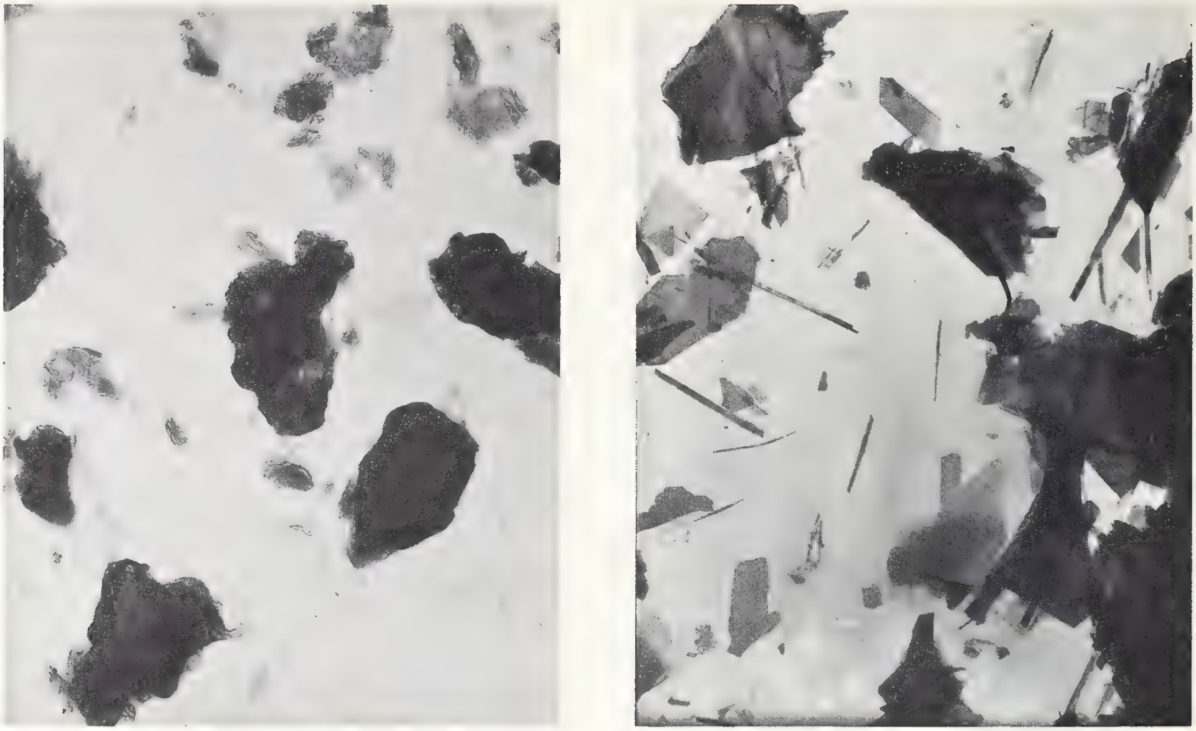
The Formation of a Better Crystallized Calcium Silicate Hydrate

It would be expected that the apparent solubility of a compound or its resistance to change caused by aggressive media would be dependent to some extent on its physical condition. For example, a finely divided form of a material would have a higher surface area and therefore should go into solution or react at a faster rate. Also, as the degree of crystallinity increases, the lattice energy of the compound also increases. This increasing lattice energy is accompanied by a decreasing tendency for a compound to undergo change, since greater energies are required for dissociation. It is reasonable to expect that the form of calcium silicate which is produced under autoclave conditions, which has a reduced surface area and better crystallinity, would exhibit greater resistance to attack than that produced under normal cure conditions.

To demonstrate this possibility, two calcium silicate hydrates were prepared. Each had a calcium to silica ratio of 1:1, and was reacted in excess water. The first sample was treated in saturated steam at 100 lb/sq in. pressure for 16 hr, while the second sample was allowed to react at room temperature for 28 days. X-ray analysis showed the first to be tobermorite or well-crystallized CSH-I, and the second poorly crystallized CSH-I. Electron microscope photographs of these two materials are shown in figure 4.

The solubility of the two products was tested in 0.1 *N* sulfuric acid, 0.5 *N* ammonium sulfate, and carbon dioxide-saturated water with a *p*H of 4, by placing 200 mg of the sample in a 4-oz polyethylene bottle and adding 50 ml of the appropriate solution. The bottles with their contents were shaken for periods of time ranging from ½ hr to 3 days. The suspensions were filtered, the residues washed with acetone, dried at room temperature, weighed, and studied by X-ray diffraction. The results are summarized in table 3.

From the data it is seen that weight change is not the prime consideration for evaluating the stability of a substance. Weight loss is indicative of solubility and weight gain indicates reaction with the environment. Therefore, when both take place together the weight change results must be accompanied by other data to obtain a



Normal Cure - 17,000X

Autoclave Cure - 17,000X

FIGURE 4. *Electron microscope photographs of normal- and autoclave-cured calcium silicate hydrate compounds.*

TABLE 3. *Laboratory corrosion tests on calcium silicate hydrate compounds made under different curing conditions*

A—Amorphous material, C—CSH-I, G—Gypsum, L—Calcium carbonate, T—Tobermorite

Time	0.1 *N* H_2SO_4				0.5 *N* $(NH_4)_2SO_4$				CO_2-Saturated water			
	Normal cure		Autoclave cure		Normal cure		Autoclave cure		Normal cure		Autoclave cure	
	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition
Hr	*Percent*		*Percent*		*Percent*		*Percent*		*Percent*		*Percent*	
½	−85.05	A+C (trace)	−63.8	T+G (trace)	−42.5	C+G (small)	−11.6	T	−6.65	C+L (small)	−8.7	T.
1		G+C (trace)	−65.5	T+G	−42.2	G+C (small)	−10.8	T	+20.8	L+C (trace)	+10.7	T+L (small).
5	−73.75	G+C (trace)							+5.5	L+C (trace)	+10.8	T+L.
24	−35.5	G	−38.5	G+T (small)	−11.0	G	−17.7	T+G (trace)	+7.2	L+C (trace)	+19.5	T+L.
72					−16.5	G	−24.15	T+G (trace)	+4.6	L+C (trace)	+11.5	T+L.

complete understanding of the effect of environment. X-ray data provide a crude measure of the breakdown of the original material and the new compounds which are forming.

General Remarks

Field test results provide a measure of the reliability of laboratory conclusions on corrosion resistance. Both field and laboratory tests show that autoclave curing improves the resistance to attack of asbestos-cement materials. The results discussed above are in excellent agreement with the conclusions of van Aardt concerning the effects of high-pressure steam curing.

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Paper VI–S2. Capillary Size Restrictions on Ice Formation in Hardened Portland Cement Pastes*

R. A. Helmuth

Synopsis

T. C. Powers' model of the pore structure of hardened portland cement paste is used to discuss the conditions that must be met for ice formation in capillaries of various sizes. It is proposed that initial ice formation in supercooled water in the capillaries occurs dendritically, just as it does in bulk water, through only those sufficiently large capillaries which are contiguous with the initially seeded capillaries. Subsequent growth of this dendritic network of ice crystals and resulting expansions during cooling depend primarily on freezing in smaller capillaries at lower temperatures. This theory is supported by the results of experiments in which freezing propagation rates and temperature rises were measured during tests with supercooled pastes, and by experiments in which dimensional changes were measured during cooling and warming through freezing temperatures.

Résumé

Le modèle proposé par T. C. Powers sur la structure des pores de la pâte de ciment portland durcie est utilisé dans la discussion des conditions nécessaires à la formation de glace dans les capillaires de différentes dimensions. Il est proposé que la formation de glace initiale dans l'eau sous-refroidie dans les capillaires se produit dendritiquement, exactement comme dans l'eau en large volume mais seulement à travers les capillaires suffisamment larges et attenant aux capillaires précédemment ensemencés. La croissance ultérieure de ce réseau dendritique de cristaux de glace et les expansions qui résultent pendant le refroidissement dépendent en premier lieu de la congélation dans les plus petits capillaires aux basses températures. Cette théorie est supportée par les résultats d'expériences dans lesquelles les vitesses de propagation de la congélation et les élévations de température étaient mesurées pendant des essais avec des pâtes refroidies, et par des expériences dans lesquelles les changements de dimensions étaient mesurés pendant le refroidissement et le réchauffement à travers les températures de congélation.

Zusammenfassung

Das Modell, welches T. C. Powers für die Porenstruktur einer erhärteten Portlandzementpaste angegeben hat, wird benutzt, um die Bedingungen klar zu machen, unter denen eine Eisbildung in den Kapillaren verschiedener Größe vorkommen kann. Es wird vorgeschlagen, daß die erste Eisbildung in unterkühltem Wasser in den Kapillaren sich dendritisch ereignet, ganz so wie sie in einer offenen Wasseroberfläche sich ereignen würde, aber doch nur in den verhältnismäßig großen Kapillaren vorkommt, die an die Kapillaren, in welchen der erste Eiskeim entstand, anstoßen. Das darauffolgende Anwachsen des dendritischen Gitters der Eiskristalle und die davon herruhrende Ausdehnung während des Kühlens hängen überwiegend vom Gefrieren in kleineren Kapillaren bei niedrigeren Temperaturen ab. Diese Theorie wird durch die Experimentalbefunde unterstützt, in welchen man die Fortpflanzungsgeschwindigkeiten des Gefrierens und die Temperaturerhöhungen in Versuchen mit unterkühlten Pasten festgestellt hat; in anderen Experimenten hat man die Dimensionsveränderungen während des Abkühlens und des Erwärmens in der Nähe der Gefriertemperaturen gemessen.

Introduction

A study of the freezing of water in hardened portland cement pastes with and without entrained air was undertaken some years ago to obtain experimental verification of T. C. Powers' hydraulic pressure hypothesis [1, 2].[1] There were some perplexing features of those data [3] which have been elucidated by subsequent experimental work. In particular, the manner in which freezing is initiated in the capillaries in the cement paste was not determined and the rates of expansion and ice formation during cooling were found to be much smaller than expected from the melting data obtained earlier by Powers and Brownyard [4]. This difference indicated the existence of certain restrictions on ice formation during cooling that required further examination. In earlier papers [3, 5], it was assumed that ice formed in capillaries *without* seeding by an existing ice phase. Examination of the nucleation and crystal-growth processes leads to a rather different view of the freezing process in the early stages of ice formation.

The manner in which freezing begins in a supercooled, moist, porous solid should resemble the freezing of supercooled bulk water. Dorsey [6] made a systematic study of the freezing of supercooled samples of bulk water in which he found that the freezing depended on the size and nature of small solid particles in the sample and on some features of the walls of the container. If there are no particles present, or if the solids are ineffective nucleating agents, supercooling to very low temperatures results.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Illinois.

[1] Figures in brackets indicate the literature references at the end of this paper.

Chalmers has studied the dendritic nature of ice formation in supercooled water. He writes [7] that the ice-water interface forms ". . . a series of separated spikes, each of which has its axis in a well defined crystallographic direction, and with branches in other equivalent directions." This arrangement results in rapidly growing, fernlike structures in supercooled water as shown in figure 1, [8].

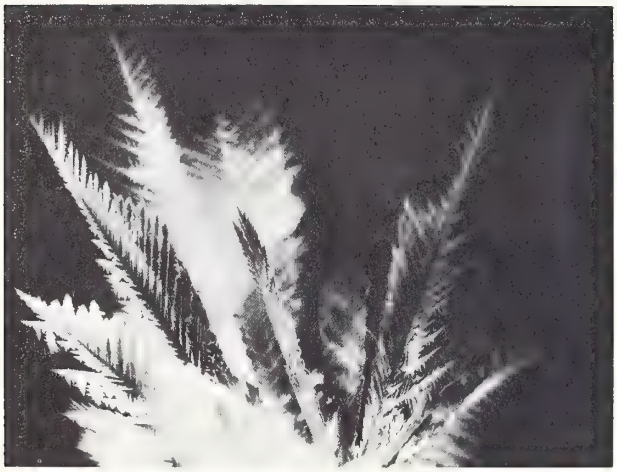

FIGURE 1. *Dendritic ice formation in supercooled water.* (Courtesy of Prof. B. Chalmers and *Scientific American.*)

Studies of the freezing of water in foods, soils, building stones, concrete, and hardened cement paste show that supercooling is commonly observed even in the presence of various solids which might be expected to serve as nucleating agents [4, 9, 10, 11, 12].

In Powers' model of cement-paste structure [13] the capillary spaces are described as the residues of originally water-filled space in the fresh cement-water mix. They are much larger than the pores between particles of cement hydration products formed around cement grains, which are called gel pores. Powers and Brownyard argued that the ice in cement pastes formed in the relatively large capillary spaces in their model of cement paste structure, but not in the small (20–40A) pores in the gel produced by cement hydration. In addition they argued that the melting temperature of any ice crystals small enough to be contained in the gel pores would prevent freezing until very low temperatures were reached.

In this study it is proposed that the water in the capillaries in cement pastes supercools before freezing because of restrictions on ice crystal growth through the pore structure and that the initial ice formation occurs dendritically through water in capillaries. After the initial freeze, the subsequent extension of the network of frozen capillaries also depends on the capillary size restrictions on ice formation. Hence, data from freezing experiments provide more information about the pore structure of the paste, as well as about the freezing process.

Theory

Porosity of Hardened Pastes

According to Powers' model of cement-paste structure all cement pastes contain gel pores which, when filled with water, contain a mass of gel water given [14] by:

$$w'_g = 0.74 w_n \tag{1}$$

in which w_n is the mass of nonevaporable water, which is essentially the water of hydration, and is commonly about 0.2 g per gram of cement for complete hydration. The prime notation on water-content symbols will be used to designate values of water-saturated pastes. The constant 0.74, which depends on the cement composition, was determined on the same Type I cement (15754) used in this study. This quantity of gel water is equivalent to 2.38 monolayers adsorbed on the solids in the paste if the surface area of the solids is taken as that determined by the BET method [15]. In addition to the gel pores, cement pastes contain much larger capillary spaces which, when filled with water, contain a mass of water w'_c. The total mass of water in a paste, saturated or not, is:

$$w_t = w_c + w_g + w_n \tag{2}$$

in which w_c and w_g are the water contents of the capillary and gel spaces, respectively, and the sum of w_c and w_g is w_e, the evaporable water. The total porosity of the paste can be divided into the porosity of the gel and the capillary porosity, p_c. Copeland [16] has shown that the specific volume of the capillary water in saturated cement pastes is 0.99, which is the value to be expected from the presence of the small quantity of alkali metal hydroxides in solution. Then the capillary porosity is given by:

$$p_c = \frac{0.99 w'_c}{V_p} \tag{3}$$

in which V_p is the paste volume.

The Capillary Saturation Coefficient

When the paste is partly dried, the remaining water distributes between capillary spaces and gel pores, but at high relative vapor pressures most of the water lost is from the capillary spaces [17]. The capillary saturation coefficient is defined as:

$$s_c = \frac{w_c}{w'_c} = \frac{w_t - w_g - w_n}{w'_t - w'_g - w_n} = \frac{w_t - 1.74 w_n}{w'_t - 1.74 w_n} \tag{4}$$

in which w'_t is the total water required to saturate the paste, and it is assumed that the gel pores remain water-saturated. If the specific volume of the capillary water is independent of this saturation coefficient, this equation also gives the volume fraction of capillary space which is filled with water.

If a cement paste is maintained in a water-saturated condition from the time it is cast

$$w'_t = w_o + 0.254 w_n \tag{5}$$

in which w_o is the original water content [16]. Hydration of the cement produces self-desiccation of the paste if it is cured in a sealed mold from the time it is cast. In such cases w_t is the original water content w_o, but w'_t is given by eq (5), so

$$s_c = \frac{w_o - 1.74 w_n}{w_o - 1.49 w_n} \tag{6}$$

for self-desiccated pastes [17].

When a water-saturated cement paste is cooled from 25 to 0 °C, moisture moves from the capillary spaces into the gel. Capillary space emptied can be filled by soaking in water. The resultant increase in weight is given [18] by:

$$\Delta w = 0.0194 w'_g + 0.0024 w'_c. \tag{7}$$

If the paste is not soaked in water, Δw is the amount by which w'_c is reduced to w_c, and eqs (4) and (7) can be used to obtain the fraction of the capillary space which is empty of water. Then

$$s_c = 1 - \frac{0.0194 w'_g + 0.0024 w'_c}{w'_t - 1.74 w_n} \tag{8}$$

for pastes cooled from 25 °C without additional water imbibition.

Supercooling and the Initiation of Freezing

Freezing of water can be initiated in any of three ways, by (a) homogeneous, or thermal nucleation [19], (b) heterogeneous nucleation, such as by oriented adsorption of water in an ice structure over a sufficiently large area on a solid surface [20], or (c) seeding with a piece of ice. At every temperature below 0 °C there is finite probability of homogeneous nucleation in any finite time interval. This probability is extremely small for the specimen size, temperature range, and time intervals considered here [21]. Specimens in this study have been supercooled to temperatures as low as −15.0 °C. There is apparently no feature of the structure of the paste which can serve as a nucleation site for ice formation at temperatures higher than this. Hence, when freezing does begin at higher temperatures it is most probably initiated by some external means, such as by seeding the supercooled water in the pores with an ice crystal. At the specimen surface an external ice crystal can seed ice formation in surface pores, but in the interior pores only ice in adjoining pores can act as seeds. Hence it seems that if seeding is necessary, ice formation must be propagated as a continuous phase through the pore structure of the paste.

Propagation of a continuous ice phase through the pore structure of the paste depends on whether ice can be formed of such size and shape as to be stable at the freezing temperature. These ideas have been discussed by Penner [22], Gold [23], and Jackson and Chalmers [24], with respect to ice formation in soils. In materials with finer pore structure the problem is complicated by the presence of an unfreezable film of water adsorbed on the solid. Powers and Brownyard showed that even when the water in the paste came to equilibrium with stress-free ice there remained u molecular layers of unfrozen water adsorbed on the solid surfaces of the hydrated cement, where u has a value of about 4.0 and varies slightly with the temperature. Hence an ice crystal in any small capillary must not only be smaller than the capillary diameter, D (assuming it is more or less circular in cross section), but smaller than $(D-2ut)$ in which t is the thickness of a monolayer of adsorbed water. Volmer [25] discussed the stability of small crystals in their melts below the normal melting point in terms of Thomson's equation, which can be written

$$T_r = T_s \exp\left(-\frac{2\sigma M}{r_c Q d}\right) \tag{9}$$

in which T_s is 273 °K, T_r is the fusion temperature of an ice crystal with radius r_c, σ is the interfacial energy between ice and water, Q is the molar heat of fusion, d the density and M the molecular weight of ice. If we take $\sigma = 10.2$ dynes/cm, $Q = 14{,}400$ cal/mole, $d = 0.917$ g/cm^2 and $M = 18.02$ g/mole, the values for r_c corresponding to the values of T_r given in table 1 can be calculated. D can then be computed as $(2ut+2r_c)$, the diameter of the capillary required to contain the smallest ice crystal stable at the temperature T_r. The value taken for t was 3.1 A which corresponds to the density of bulk water, which is believed to be at least approximately correct. If the ice crystal is a dendrite, r_c is the radius of a sphere inscribed in the crystal at the growing end. It is this end which must penetrate the constrictions in the pore structure.

Table 1. *Size of capillaries required for propagation of ice formation at temperature t_r*

$T_r - T_s$	u	ut	r_c	$(2ut+2r_c)$
°C		A	A	A
−2	[a] 4.5	13.9	90	208
−6	4.0	12.4	29	83
−10	3.7	11.5	18	59
−15	3.2	9.9	12	44
−20	[a] 2.7	8.4	9	35

[a] By extrapolation.

In supercooled bulk water, freezing is known to occur dendritically. In a porous solid the crystal growth must be restricted not only by the crystal habit of the ice but also by the solid surfaces which the dendrites encounter during their growth. The lateral growth of the dendrites is much slower than the longitudinal growth [26] because the latent heat of crystallization is dissipated into the supercooled water much more rapidly from the tip of the dendrite than along its length. Then the initial rapid formation of ice should cease when the dendrites have penetrated all the sufficiently large capillaries contiguous with the initial ice seed. The immediately subsequent ice formation should be much slower.

The initiation of freezing in a supercooled paste at some temperature, T_f, should produce rapid dendritic growth of ice crystals which must be at least as large as those given by eq (9). These dendrites can grow through only those constrictions in the interconnected capillary system which are larger than this size. During this rapid freezing heat is liberated which raises the temperature of the supercooled paste by ΔT_f to a temperature, T_m, at which the size of thermodynamically stable dendrites is larger than any remaining constrictions in the unfrozen water-filled capillaries. At this temperature the rapid dendritic growth must cease, and only the much slower lateral growth can occur. If freezing is initiated at a temperature at which the ice crystals can be, by eq (9), only slightly smaller than the constrictions in the largest capillaries, only a very limited network of capillaries will freeze. In this case the temperature rise will be very small. Alternatively, if freezing is initiated at a considerably lower temperature, ice crystals can grow through smaller constrictions and more ice can form in the initial freeze. If the largest water-filled capillaries are sufficiently numerous the temperature will rise to the same temperature as it did when freezing began at the higher temperature. The maximum temperature reached, T_m, should be independent of the initial freezing temperature, T_f, or:

$$T_m \neq f(T_f) \tag{10}$$

if the largest water-filled capillaries are sufficiently numerous. If the largest capillaries are *not* sufficiently numerous, they will all be frozen at some temperature lower than T_m. In the unfrozen smaller capillaries, freezing can occur only at lower temperature; therefore, the freezing will stop at a temperature lower than T_m.

The heat liberated by this rapid ice formation is $C_p \Delta T_f$ per gram of specimen, in which C_p is the specific heat of the paste. If it is assumed that the heat liberation is so rapid that the heat loss to the specimen surroundings is small enough to be neglected during the time of the temperature rise, the mass of frozen water must be:

$$w_f = \frac{C_p \Delta T_f}{q} (w_t + c) \tag{11}$$

in which q is the heat of crystallization of 1 g of ice, c is the mass of cement, and $(w_t + c)$ is the mass of the paste. If w_f is much smaller than w_t, C_p may be regarded as a constant.

Since the dendritic structure is a very open one, only a small amount of the water in the frozen capillaries should freeze initially. Then eq (11) can be used to obtain w_f and we should expect $w_f/w_{cf} \ll 1$ for the initial ice formation, where w_{cf} is the water content of the partially frozen capillaries. Though w_{cf} is unknown, we know that $w_{cf} \leq w_c$ and we should expect:

$$\frac{w_f}{w_c} \ll 1 \tag{12}$$

if the growth is dendritic. If eq (12) is found to be true it does not necessarily mean that the growth is dendritic because eq (12) could be true even if $w_f/w_{cf} \sim 1$, if only a few capillaries were frozen.

Experimental Procedures

The specimen casting, curing, and analytical methods have been described in detail elsewhere [18]. All pastes used in this study were free of entrained air. The cement paste specimens on which extensometer measurements were made were cast in molds consisting of 25-cm lengths of 29-mm glass tubing with a 12-mm rubber core mold fitted axially in the glass cylinder between the rubber stoppers at each end. The test specimens were 7.6-cm and 2.5-cm lengths cut from the hardened-paste hollow cylinders.

Length changes of the hollow cylinders were measured with a calibrated extensometer built around a transducer made by Statham Laboratories as previously described [18]. During tests the extensometer was partially submerged in a 4-liter temperature-control bath so that the specimen was completely immersed in kerosene and the transducer was well up in the room air. The kerosene used as the bath fluid in the first experiments had been dried by shaking with flake calcium chloride (for Wagner turbidimeter use) and probably contained a small amount of this salt. The presence of the salt had a considerable effect on the freezing behavior of the specimens, and it was found necessary to extract water soluble impurities from the kerosene. This was done by adding water to the bath, emulsifying it in the kerosene with a high speed stirrer, allowing it to settle to the bottom where it coalesced, and removing it with a suction tube. This operation was repeated whenever new kerosene was added to maintain the bath level after it was realized that this procedure would inhibit supercooling. The results presented were obtained in kerosene that had been so treated, unless otherwise noted.

The special experiments performed to measure the rate at which the initial freeze propagated through the specimens were made with specimens which were cast without hollow cores. Only specimens 3–9b, 3–14b, 3–20b, 76_1, 78_1, 80_1, 81_1, and

81_2 were of this group. The three water-saturated specimens used for measurements of freezing propagation rates, 3–9b, 3–14b, and 3–20b were cut from solid cylinders of paste cured under water for 7 yr at 23 to 25 °C. After the mold was removed they were cut to a length of 110 mm. Four holes for thermocouples were drilled in the specimens with a No. 54 (1.397 mm) drill. The holes were 9 mm deep, perpendicular to the cylinder axis, and situated 29 mm apart along a line parallel to the axis. The first and fourth holes were equally distant from the ends. The specimens were stored in limewater at 0 °C for 4 days before the tests, to insure water saturation at the freezing temperature. Before immersion in the bath, the specimens were wiped free of water and copper-constantan thermocouples made with No. 30 wire were placed in the drilled holes. The thermocouple leads were wrapped so that they fitted snugly in the ends of the holes. Ice formation in the bath and on any surface film of water on the specimen was prevented in these experiments by emulsifying 40 ml of 2 molal calcium chloride solution in the bath. It is believed that the concentration of salt in any remaining film of water on the specimen increased enough before the initiation of freezing to preclude ice formation in any such film.

In each of the measurements of propagation rates in water-saturated pastes the specimens were suspended with a burette clamp in the kerosene temperature-control bath at about +1 °C. The bath was cooled at 0.5 °C/min to freezing temperatures no lower than −8.5 °C. Freezing was initiated by touching the top end of the specimen with a piece of ice held with forceps. The position of the freezing wave front was taken to be between two thermocouples when one had indicated freezing and the next farther away from the seeded end had not. The distance between the thermocouples and the seeded end was known, and the recorder channel printing at the time of the seeding was noted, which defined the time of seeding. From these data it was possible to compute the average rate of advance, or rather the upper and lower limits, because of the uncertainty of the position of the wave front between two thermocouples. In most cases the rate was so great that only a lower limit could be determined.

The propagation rate measurements with the self-desiccated specimens 76_1, 78_1, 80_1, 81_1, and 81_2, were done in much the same way. These specimens were cured at 23 °C. After they were removed from the stoppered molds care was taken to prevent moisture loss by keeping them either in screw-capped jars or wrapped in tin foil, with only momentary exposure to room air during transfer operations. Ignition loss determinations showed no indication of drying during the preparatory manipulations. The geometry of these specimens was similar to that of the water-saturated specimens with the exception that the holes were 25 mm apart, 15 mm deep, and made with a No. 60 (1.016 mm) drill. The thermocouple junctions were at the bottom of these holes and therefore on the axis of the cylinder since the specimens were 29 mm in diameter.

After fitting the thermocouples in the holes, each specimen was mounted in the bath at 23 °C, cooled at 0.5 °C/min to +5 °C, held there about 10 min, then cooled at 0.5 °C/min to about −8 °C, then warmed at 1 °C/min to +5 °C, and held there again for about 10 min. This cycle was repeated two to five times.

Experimental Results

The Initial Formation of Ice in Hardened Pastes

In most of the freezing experiments made in this study, freezing was not initiated by any deliberate operation but was left somewhat to chance except for control of the temperature and certain other features of the environment. In the first experiments, the specimens supercooled to temperatures ranging from −5 to −15 °C before freezing began. Freezing was indicated by an abrupt expansion and temperature rise. After about 8 weeks of daily testing it was found that the initial freezing temperatures had gradually increased to about −1.5 °C, and this temperature was independent of the porosity or other characteristics of the different specimens. It was also observed that some water (perhaps 50 ml) had accumulated in the kerosene bath by dripping of condensed atmospheric moisture from upper parts of the bath cooling coil. This water, which was emulsified in the kerosene by the stirrer during tests and settled out between tests, had apparently inhibited supercooling of the water in the specimens. At temperatures below 0 °C this water in the bath formed frazil-like ice that tended to collect in a mass of fine crystals around the extensometer.

Some experiments were performed to test whether or not the frazil ice in the bath was seeding ice formation in the specimens. In these experiments it was found that the hardened pastes froze at about −1 °C when water-soluble impurities were extracted from the kerosene, as described above, if there was some free water in the kerosene, and that these same pastes supercooled to temperatures as low as −7.0 °C when concentrated NaCl solutions were emulsified in the kerosene.

To investigate this apparent seeding at the specimen surface and propagation of ice formation to the specimen interior in the preceding experiments, additional experiments were performed to measure the rate of propagation of ice formation through supercooled pastes after touching one end with a piece of ice. The results presented in table 2 were obtained with 7-yr-old, water-saturated specimens. For comparison, the results obtained by Hillig and Turnbull [27] for ice-crystal growth rates in supercooled water in glass capillary tubes and by Lindenmeyer, Orrok, Jackson, and Chalmers [28] for free growth in supercooled bulk water are given corresponding to the temperature, T_f. Both of these refer to growth perpendicular to the c-axis of ice, i.e., the rapid growth direction.

Table 2. *Freezing propagation rates in supercooled water-saturated hardened cement pastes*

Specimen	w_t/c	w_n/c	T_f	T_m	Propagation Rates (mm/sec)			
					At least	At most	Linden-meyer et al.	Hillig and Turnbull
			°C	°C				
3-9b	0.640	0.221	−4.9	−4.0	8.7	------	10	23
3-14b	.541	.219	−2.7	−1.5	5.1	11	2.5	8.6
3-14b	.541	.219	−5.4	-------	8.1	------	13	27
3-20b	.477	.219	−2.6	−2.2	11	------	2.4	8.2

Specimens 3–9b and 3–14b were found to contain cracks after the tests of table 2. To determine whether freezing propagation could be detected even when such damage could not occur, self-desiccated pastes with capillary saturation coefficients less than 0.91 were used. (Even these pastes were sometimes damaged by freezing when greatly supercooled. However, in such cases the maximum temperature reached was the same during the first freeze, when supercooling was slight, as during subsequent freezes when the supercooling was great. Therefore, the damage incurred could not have had much effect on the initial freezing process. Perhaps the cracks did not result from stresses developed directly by ice formation but resulted from thermal stresses across the freezing wave front. These may have been quite high when the supercooling was great.) Figure 2 shows the strip chart record of the thermocouple outputs during the sixth freeze of specimen 76_1. The results of computation of the propagation velocity from the strip chart data and the specimen water contents are given in table 3. In some cases the upper and lower limits on propagation rates coincide because the recorder happened to record just at the time the temperature was changing at a thermocouple and this defined the position of the wave front much more exactly than in the other cases.

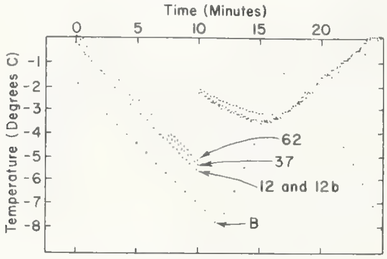

Figure 2. *Strip chart record of thermocouple EMF's during freezing of specimen 76_1.*

B indicates thermocouple in the bath; 12, 37, 62, and 12b indicate the thermocouple in the specimen, 12, 37, and 62 mm from the top and 12 mm from the bottom, respectively.

Table 3. *Freezing propagation rates in supercooled self-desiccated hardened cement pastes*

Specimen	w_t/c	w_n/c	Freeze	Temp. of bath	Propagation Rates mm/sec.			
					At least	At most	Linden-meyer et al.	Hillig et al.
				°C				
76_1	0.469	0.118	1	−5.0	3	4.6	11	24
			2	−4.8	3	4.6	10	22
			3	−6.9	7	14	23	41
			4	------	------	------	------	------
			5	−4.4	2.1	3.5	8	19
			6	−7.1	14	------	29	43
78_1	.460	.120	1	------	------	------	------	------
			2	−5.2	3	4.6	12	25
			3	−8.0	14	------	32	54
			4	------	------	------	------	------
			5	−6.8	14	14	22	40
80_2	.457	.138	1	------	------	------	------	------
			2	−8.1	7	7	33	55
			3	------	------	------	------	------
81_1	.550	.134	1	------	------	------	------	------
			2	------	------	------	------	------
			3	−5.3	7	14	12	26
			4	−7.0	14	------	27	42
			5	−4.4	7	7	8	19
81_2	.561	.152	1	------	------	------	------	------
			2	−5.8	5	5	15	31
			3	−7.1	7	7	29	43
			4	------	------	------	------	------
			5	−7.1	7	7	29	43
			6	------	------	------	------	------

The purpose of the experiments of table 3 was only secondarily to measure the propagation rates. The primary purpose, and the reason for placing the thermocouples so deep in the specimen, was to measure the maximum temperature reached during the rapid initial formation of ice. These results are plotted in figure 3 versus the initial freezing temperature. Table 6 contains a summary of all the T_f and ΔT_f measurements presented in the tables and figures in this report.

Dimensional-change measurements made during freezing with supercooling reveal that the expansion rate during the initial freeze is rather small

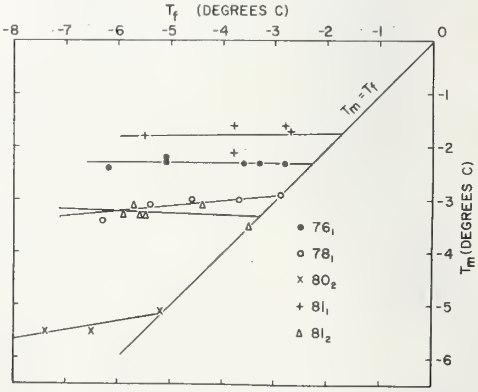

Figure 3. T_m, *maximum temperature reached during initial freeze of supercooled cement pastes frozen at different temperatures* T_f.

even though the rate of ice formation, as indicated by the rapid rise in the specimen temperature, is much greater than during the subsequent progressive expansion. Figures 4 and 5 show the temperature-versus-time and length change-versus-time curves for specimens 55_2t and 63_2t. These 0.45 water-cement ratio pastes were cured at 5 °C for 4 days. Specimen 55_2t was cured without additional water and thus became somewhat self-desiccated. Specimen 63_2t was cured with lime-water in the hollow core of the specimen, which maintained water saturation during hydration. The beginning of freezing is indicated in each case by an expansion and a coincident break in the temperature-time curve.

Table 4 gives the initial freezing results of three nearly completely hydrated specimens of high water content. These specimens were cured in water at room temperature and were of approximately equal porosities. Water-soluble impurities had not been extracted from the kerosene bath at the time the tests of specimens HVb and AAVb were made. The initial expansions increased with the amount of supercooling which preceded freezing. In each case, further cooling produced much larger total expansions. The complete freezing-thawing results for a similar paste are given in figure 12. Specimen AAVb was frozen again 2 days after the test of table 4. It supercooled to −15.0 °C before the second freeze.

Table 4. *Expansions produced by freezing of supercooled pastes*

Specimen	w_t/c	w_n/c	T_m	T_f	ΔT_f	Initial expansion
			°C	°C	°C	
IVLt	0.683	0.220	−0.6	−0.9	0.3	0×10^{-6}
HVb	.692	.228	−3.9	−4.8	0.9	100×10^{-6}
AAVb	.721	.233	−7.1	−8.8	1.7	$>320\times10^{-6}$

Three typical cases of freezing of pastes of low porosity are shown in figure 6. Water-soluble impurities had not been extracted from the kerosene bath at the time the tests of specimens SVb and UVb were made. Specimen SVb was cooled at 0.25 °C/min from 22.8 °C, and test conditions were such that it supercooled to −6.0 °C before freezing. The plot shows both a 40 x 10^{-6} expansion and an increase in the temperature of the interior of the specimen to −5.4 °C. Specimen UVb was cooled at 0.25 °C/min from 22 °C and supercooled to only −1.4 °C before freezing. An expansion of 20 x 10^{-6} accompanied a temperature rise to −1.0 °C. No perceptible temperature rise occurred when specimen 9_1b was frozen. Freezing at −0.7 °C was apparent because of an increased temperature gradient in the specimen and an expansion of 10 x 10^{-6}.

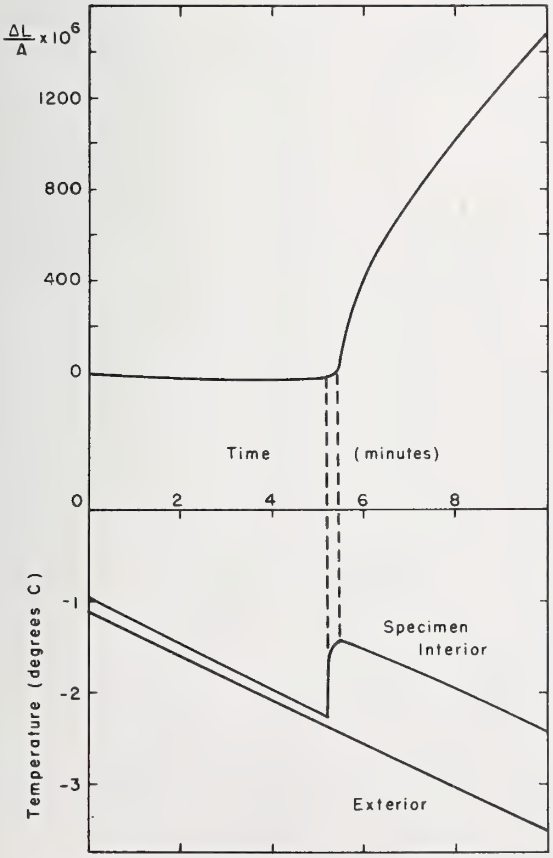

Figure 4. *Results of freezing specimen 63_2t.*

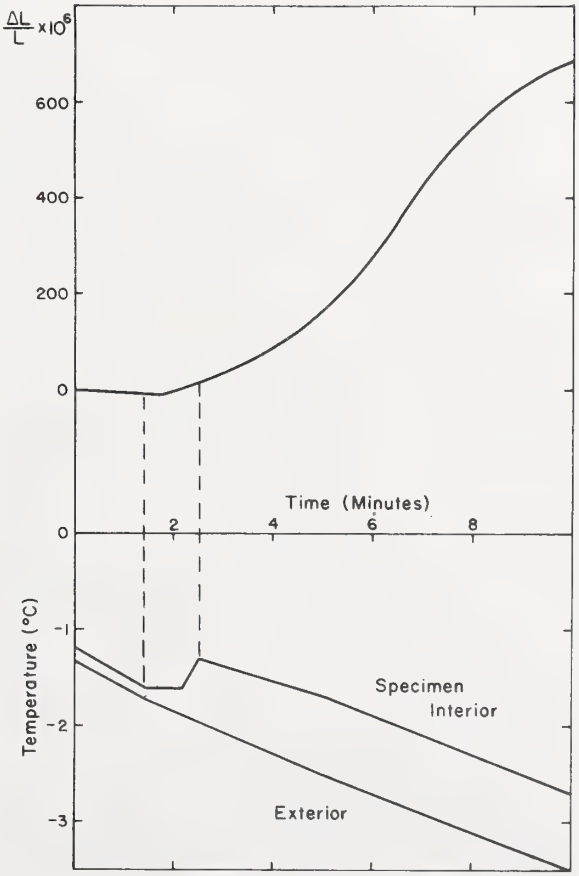

Figure 5. *Results of freezing specimen 55_2t.*

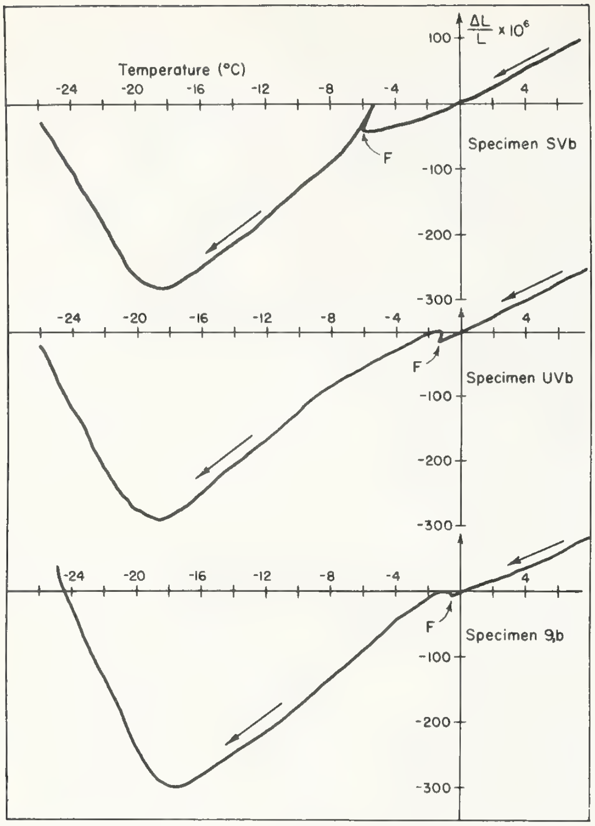

FIGURE 6. *Freezing curves of 0.45 water-cement ratio pastes.*

Cooling at 0.25 °C/min. F indicates the beginning of freezing.

These specimens were all of 0.45 water-cement ratio. A similar specimen, TVt, was subjected to the same kind of test after storage in ice water for 4 days. The initial expansion of 100 x 10^{-6} resulted in a temperature rise from −2.7 to −1.4 °C. The curve was otherwise very similar to that of specimen SVb.

Ice Formation Immediately Subsequent to the Initial Freeze

Figure 7 shows the results of length change and temperature measurements obtained during freezing tests of five water-soaked cement pastes. The specimens were 2.5-cm sections of hollow cylinders of pastes of 0.45 water-cement ratio, cured at 5 °C with water in the central core for periods ranging from 7.8 to 870 days. Each of the specimens was cooled at 1 °C/min from room temperature (to which it had warmed during preparation for the test) to +1 °C where it was held long enough to reach constant length. Then it was cooled at 0.25 °C/min to −10 °C, or even lower temperature.

More detailed information obtained with specimen 57_1t of figure 7 is given in figure 8 which shows ΔT, the difference between the temperature of the specimen interior and the bath temperature. This difference is directly related to the rate of ice formation in the specimen since the cooling

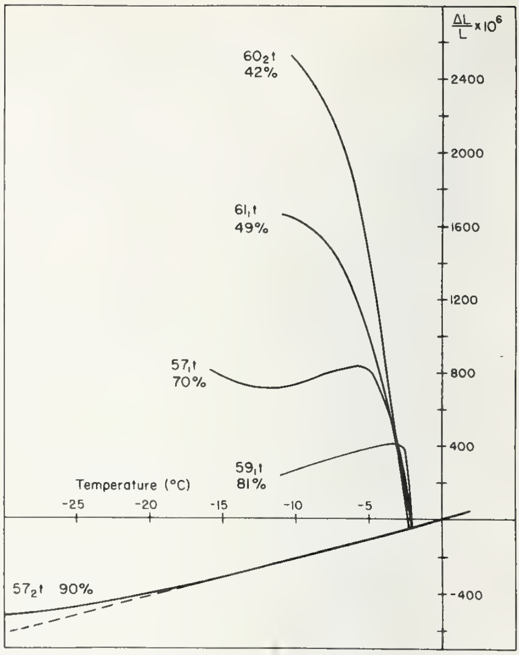

FIGURE 7. *Freezing expansions of water-soaked pastes with percent hydration as indicated by* w_n/c.

$w_o/c=0.45$.

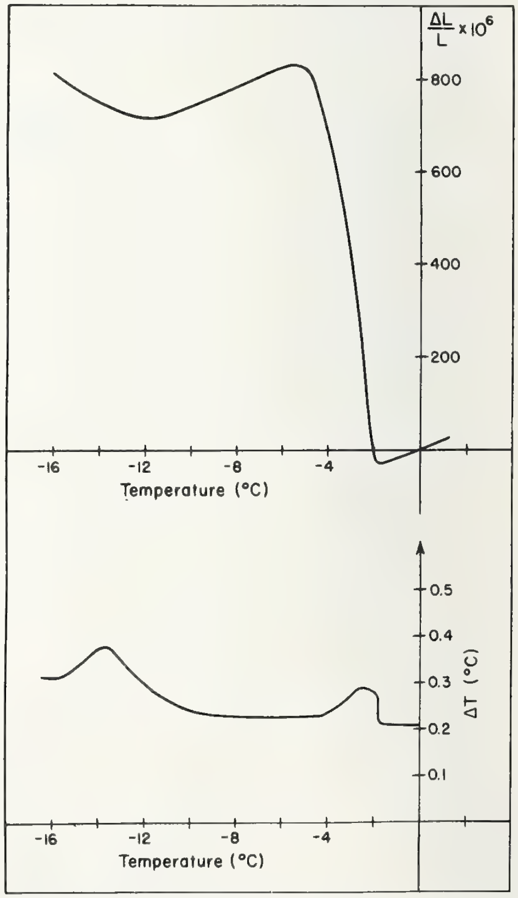

FIGURE 8. *Results of freezing specimen 57_1t.*

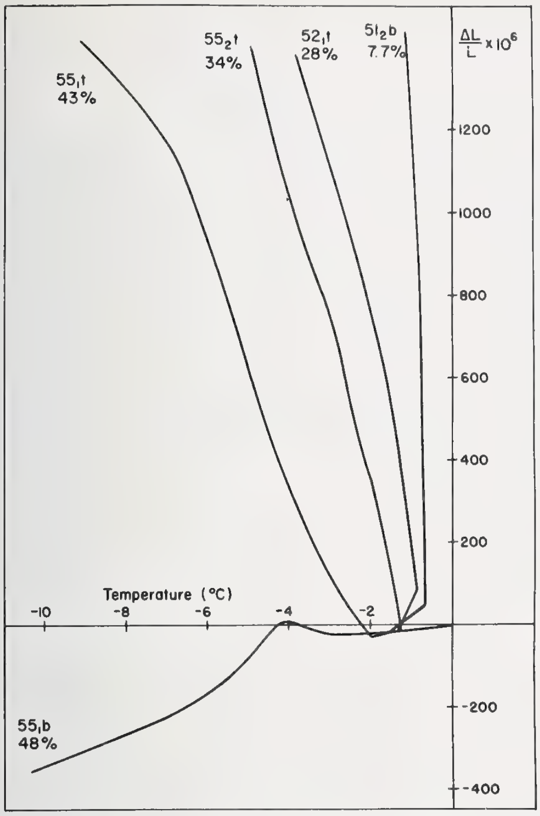

FIGURE 9. *Freezing expansions of self-desiccated pastes with percent hydration as indicated by* w_n/c.

$w_o/c=0.45$.

was done at a constant rate and other conditions remained essentially constant.

Figure 9 shows the results of freezing tests of self-desiccated pastes of $w_o/c=0.45$ cured 1 to 10 days at 5 °C. Each of the 2.5-cm specimens was cooled at 1 °C/min from room temperature (to which it had warmed during preparation for the test) to +1 °C and allowed to come to constant length. Then it was cooled at 0.25 °C/min to −10 °C and the temperature again held constant. The freezing expansion was almost entirely eliminated after 10 days of hydration, at which w_n/c was 0.110. In fact, freezing produced shrinkage in addition to thermal contraction after the small expansion. In the test of specimen 55$_1$t the expansion did not begin until −2.0 °C was reached, though a change in the temperature gradient and slope of the contraction curve indicated that freezing had begun at −0.7 °C. In the test of specimen 55$_1$b freezing began at −0.9 °C though the progressive expansion did not begin until −3.0 °C. These results are shown clearly in figures 10 and 11.

Progressive Extension of the Initially Formed Ice Network

Figures 12, 13, and 14 show the results obtained with 7.6 cm, nearly completely hydrated specimens of various w_t/c which were frozen and thawed at 0.25 °C/min. These specimens had been thoroughly leached of soluble alkalies. The fact that the large progressive expansions in these tests began at low temperatures for pastes of low

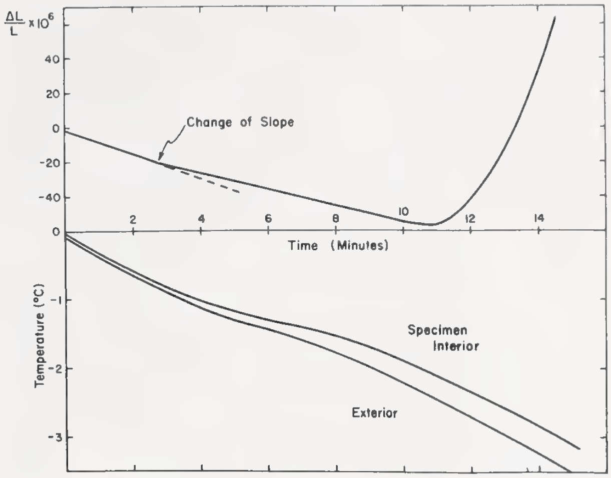

FIGURE 10. *Details of the freezing curves of specimen 55$_1$t.*

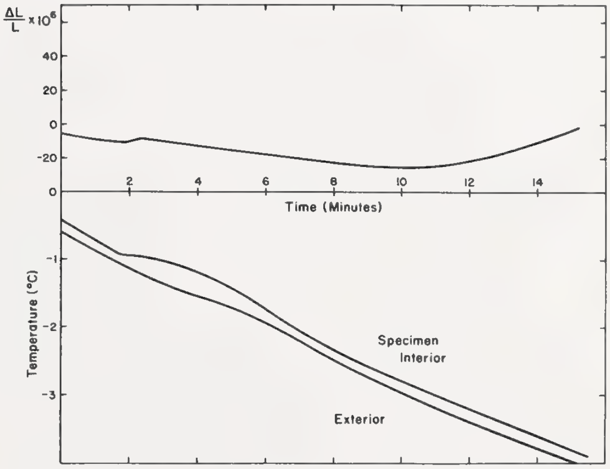

FIGURE 11. *Details of the freezing curves of specimen 55$_1$b.*

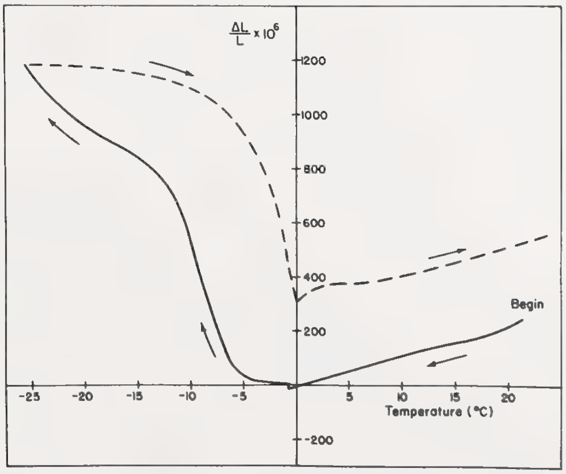

FIGURE 12. *Freezing cycle test at 0.25 °C/min.*

Specimen IVLb; w_t/c was 0.610, w_n/c was 0.220.

porosity was a general feature of all the tests made with water-soaked pastes without entrained air. One group of specimens was cured in a closed tank at 23 °C by standing in about 3 cm of water with the hollow core of each specimen packed with wet paper tissues. Self-desiccation was prevented because this wick kept the specimen surface wet during hydration. Figure 15 shows the relationship between the temperature at which the large progressive expansion (not the "pip" signifying initial ice formation) began and the capillary porosity of the most porous (upper) part of the test specimen. The figure shows results for pastes at different w_n/c and different cooling rates.

The results of testing a mature paste cured at 23 °C in a sealed mold to permit self-desiccation are given in figure 16. The original water-cement ratio was 0.432, so the results may be compared with those of the water-saturated pastes of figure 6.

The total water contents, nonevaporable water contents, and curing methods of specimens referred to individually in the various figures and tables are compiled in table 5.

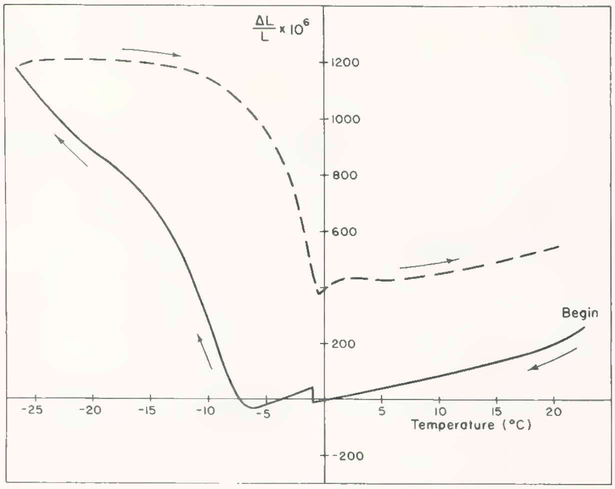

Figure 13. *Freezing cycle test at 0.25 °C/min.*

Specimen HVLb; w_t/c was 0.583, w_n/c was 0.222.

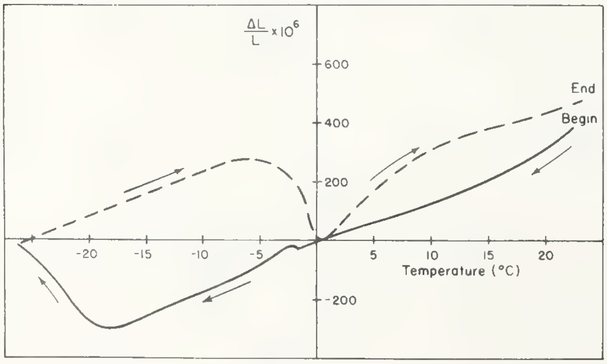

Figure 14. *Freezing cycle test at 0.25 °C/min.*

Specimen KVLt; w_t/c was 0.505, w_n/c was 0.215.

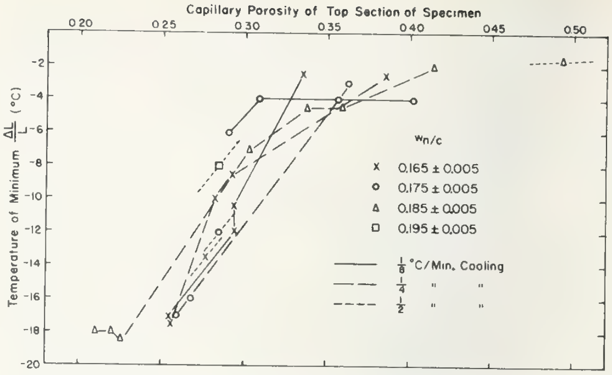

Figure 15. *Effect of capillary porosity on the temperature of the beginning of progressive expansion.*

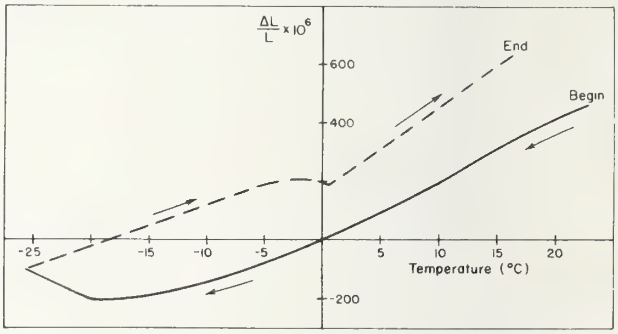

Figure 16. *Freezing cycle test of self-desiccated specimen 29_1b.*

w_t/c was 0.432 and w_n/c was 0.199. Cooling and warming at 0.25 °C/min.

Table 5. *Summary of specimen data*

Specimen	w_t/c	w_n/c	Curing [b]	Curing temperature
				°C
AAVb	0.721	0.233	C+L	23
HVb	.692	.228	C+L	23
SVb	.49 [a]	.225	C+L	23
TVt	.49 [a]	.224	C+L	23
UVb	.49 [a]	.225	C+L	23
HVLb	.593	.222	C+L	23
IVLt	.683	.220	C+L	23
IVLb	.610	.220	C+L	23
KVLt	.505	.215	C+L	23
9_1b	.484	.168	W	23
29_1b	.432	.199	S.D.	23
51_2b	.440	.018	S.D.	5
52_1t	.440	.064	S.D.	5
55_1t	.446	.099	S.D.	5
55_1b	.429	.110	S.D.	5
55_2t	.440	.077	S.D.	5
57_1t	.488	.162	C	5
57_2t	.483	.207	C	5
59_1t	.495	.187	C	5
60_2t	.465	.097	C	5
61_1t	.472	.113	C	5
63_2t	.443	.072	C	5
76_1	.469	.118	S.D.	23
78_1	.460	.120	S.D.	23
80_2	.457	.138	S.D.	23
81_1	.550	.134	S.D.	23
81_2	.561	.152	S.D.	23
3-9b	.640	.221	M	24
3-14b	.541	.219	M	24
3-20b	.477	.219	M	24

[a] Estimated from orignal water-cement ratio and w_n/c.

[b] *C*=Cured with water in hollow core of specimen.
W=Cured with a water-soaked wick in the specimen core.
S.D.=Cured in a sealed mold to permit self-desiccation.
L=Leached of soluble alkalies by storage in 60 liters of limewater for 18 mos.
M=Solid cylinders cured under water in mold.

Discussion of Results

The Initial Formation of Ice in Hardened Pastes

Three kinds of evidence have been presented to show that ice formation in the paste requires seeding and is propagated as a continuous phase through the interconnected pores of the paste.

First, it was shown that preventing ice formation in the bath emulsion around the specimen prevented freezing of the water in the interior of the paste specimens to temperatures as low as −15 °C. It seems reasonable to suppose that the frazil-ice crystals formed in the bath, seeded ice formation in water in surface pores of the specimens, and that supercooling was pronounced in the early tests because (a) the kerosene originally contained a little calcium chloride which depressed the "freezing point" of any water in the bath, and (b) there was so little water in the bath that the probability of an ice crystal forming and striking the specimen was not very large until temperatures lower than about −5 °C were reached.

Second, it was shown that touching a supercooled specimen with a piece of ice produced ice formation throughout the specimen, and in fact the speed of propagation of freezing could be measured. The results presented for water-saturated pastes agree reasonably well with those given by Hillig and Turnbull [27] for ice growth rates in glass capillary tubes and by Lindenmeyer, Orrok, Jackson, and Chalmers [28] for free growth of ice crystals in supercooled bulk water. The latter authors found that the growth rate was influenced strongly by the thermal conductivity of the supporting medium, presumably because the formation of ice was limited by the extraction of the latent heat of crystallization, so Hillig and Turnbull's results are thought to be more appropriate for comparison with cement-paste results. The propagation speeds measured with the self-desiccated pastes were only about one-tenth that found in saturated pastes. Perhaps this difference occurred because the thermal conductivity of the partially dried pastes was less than that of the saturated pastes and because the ice formation may have followed a more tortuous path through the pore structure of the dried pastes than through the water-saturated pastes.

Third, additional evidence that the initial freezing propagation must have occurred through the pore structure of the paste was shown in table 4 and figure 6. Although the abrupt temperature rise and expansion are quite small when supercooling is slight, they do indeed indicate the beginning of freezing of water in the pores of the specimen, because increasing the porosity increases both the expansion and the temperature rise when the supercooling is great. Such variation could hardly be explained in terms of freezing of a film of water on the specimen surface. However, since specimens as porous as those in table 4 were always badly damaged in the freezing tests, it is conceivable that freezing occurred in the interior only through cracks opened up by freezing in surface pores. For this reason results of tests with pastes of low porosities were given in figure 6. It is not thought that such specimens were damaged by the initial freeze because even after large expansions at −25 °C these specimens showed no permanent dilation, and visual inspection revealed no cracks. The results with the self-desiccated pastes of figures 3 and 5 and table 3 also indicated that freezing occurred in the interior of the specimens, and such pastes are not usually damaged by freezing. This point is also substantiated by similar results obtained with pastes containing closely spaced, entrained air voids [3]. Such pastes show initial freezing "pips" indicating ice formation in the specimen, but they show no evidence of damage by freezing.

The computation of the propagation speed from the distance between thermocouples and the measured time interval is perfectly straightforward if the wave front shape is nearly planar or if the thermocouples are near the surface, as in the results in table 2. However, if the wave front is far from planar, the shape of the wave front has an effect on the velocity along the axis because of propagation along the specimen surface. During these tests the temperature of the surface was about 1.5 °C lower than that along the specimen axis. According to the results of Lindenmeyer, Orrok, Jackson, and Chalmers, ice-crystal growth should be about twice as fast at the temperature of the specimen surface as at the temperature along the axis. Hence the wave along the surface should get far ahead of the wave front proceeding down the axis. At some distance from the seeded end there should develop a steady state wave front configuration which propagates at the rate of the surface wave. Then the rate along the axis varies along the specimen and the average rate is *not* that characteristic of the temperature along the axis. We can, however, compute the propagation rate *along the surface* by consideration of the geometry of the specimen and an estimate of the shape of the wave front. The estimate is believed to be justified because the rates computed in this way have about the same temperature dependence as the rates measured by Lindenmeyer, et al. These computed rates correspond to the temperature of the surface, or the bath temperature, and not the specimen interior temperature.

Powers, Copeland, and Mann [29] concluded from a study of the permeability of hardened pastes that the originally water-filled space in the fresh mix became individual capillary cavities separated by cement gel produced by hydration unless the water-cement ratio exceeded 0.70, in which case they remained as part of a continuous, interconnected network of capillaries. However, the freezing-propagation results indicate that even mature pastes of 0.45 water-cement ratio contain at least a few continuous capillaries. Simple calculations indicate that these few continuous capillaries would not be detectable by permeability measurements of the kind reported by Powers, Copeland, and Mann, except perhaps in pastes of very low porosity.

Figures 2, 3, 4, 5, 6, 8, and 9 show that in pastes containing enough water there is an initial rapid formation of ice which produces a rapid temperature rise, ΔT_f. Ice formation then continues at a much lower rate which depends partly on the rate of heat extraction. In some nearly completely hydrated pastes, such as in figures 8, 13, and 14, the ice formation virtually ceases after the rapid initial freeze and some immediately subsequent ice formation. Equations (1), (2), and (11) were applied to various results to calculate w_f/w_c from the specific heats and temperature rise in the initial freeze. The specific heats of the pastes were estimated from data given by Siegmann [30] and are tabulated in table 6 with the calculated values of w_f and w_f/w_c. The values of w_f/w_c calculated for the initial freeze are all quite small, the greatest being 0.109 for specimen 76_1 when it was supercooled to −6.2 °C before freezing. Since the w_f/w_c values are all so small, these provide direct evidence that some aspect of the paste structure imposes a restriction on the amount of initial ice formation. We may conclude that either very few of the capillaries are frozen, or that very little ice forms in the capillaries that do freeze, or that both of these possibilities are true. The results are also consistent with the hypothesis that the initial ice formation is dendritic because the immediately subsequent ice formation is much slower than the initial freezing.

In the section on theory it was proposed that if the largest capillaries are sufficiently numerous, rapid ice crystal growth should continue through these capillaries until a T_m characteristic of this capillary size is reached, and this T_m should not depend on T_f, the initial freezing temperature. The results in figure 3, obtained with immature self-desiccated specimens, show that such independence is observed in these pastes. This provides additional evidence that ice formation is restricted by the sizes of the capillaries in the paste.

The cessation of the rapid formation of ice in the initial freeze cannot readily be explained in terms of formation of a solution of the concentration required for a local equilibrium between the ice and solution in the capillaries. If such concentrated solutions were formed in the initial freeze we should expect w_f/w_c to be greater when ΔT_f was greater, which means the unfrozen solution would be more concentrated and T_m would be lower. However, T_m could not then be independent of T_f unless w_f/w_c was very small in every case, which would mean that T_m would have to be very close to 0 °C. Since the observed values of T_m are not close to 0 °C we must conclude that rapid ice formation ceased for some other reason.

Table 6. w_f/w_c *Calculated from* ΔT_f *and* C_p

Specimen	T_f	ΔT_f	C_p	w_f	w_f/w_c
	°C	°C	cal/g of paste	mg/g of paste	
AAVb	−7.1	1.6	0.48	9.6	0.049
HVb	−3.9	0.9	.46	5.2	.029
SVb	−5.4	.6	.39	2.9	.045
UVb	−1.0	.5	.39	2.4	.030
HVLb	−.9	.4	.43	2.1	.015
IVLt	−.5	.4	.46	2.3	.011
IVLb	−.6	.4	.44	2.2	.014
KVLt	−1.8	.0	.40	0	.000
9_1b	−.8	.0	.41	0	.000
51_2b	−1.5	.8	.42	4.2	.012
52_1t	−1.4	.5	.41	2.6	.009
55_1t	−.7	.0	.39	0	.000
55_1b	−1.0	.1	.38	0	.000
55_2t	−1.6	.3	.40	1.5	.005
57_1t	−1.8	.0	.41	0	.000
57_2t	−3.4	.1	.42	.5	.006
59_1t	−2.2	.2	.41	1	.009
60_2t	−1.8	.2	.42	1	.005
61_1t	−2.4	.0	.41	0	.000
63_2t	−2.2	.8	.41	4.1	.019
76_1	−3.6	1.3	.41	6.7	.037
	−3.3	1.0	----------	5.1	.028
	−5.1	2.8	----------	14.4	.081
	−6.2	3.8	----------	19.5	.109
	−2.8	.5	----------	2.6	.014
	−5.1	2.9	----------	14.9	.083
78_1	−2.9	.0	.40	0	.000
	−3.7	.7	----------	3.5	.020
	−6.3	2.9	----------	14.5	.084
	−4.6	1.6	----------	8.0	.046
	−5.4	2.3	----------	11.5	.067
80_2	−5.2	.1	.40	.5	.003
	−6.5	1.0	----------	5.0	.033
	−7.4	1.9	----------	9.5	.064
81_1	−3.8	1.7	.43	9.1	.044
	−2.7	1.0	----------	5.3	.026
	−3.8	2.2	----------	12.4	.061
	−5.5	3.7	----------	19.9	.097
	−2.8	1.2	----------	6.5	.032
81_2	−3.5	.0	.43	0	.000
	−4.4	1.3	----------	7.0	.037
	−5.5	2.2	----------	11.8	.062
	−5.9	2.6	----------	14.0	.074
	−5.6	2.3	----------	12.4	.065
	−5.7	2.6	----------	14.0	.074
3-9b	−4.9	.9	.47	5.3	.034
3-14b	−2.7	1.2	.43	6.4	.061
3-20b	−2.6	.4	.41	2.0	.031

The specimens of table 4 were all of high porosity and water saturated at 23 °C, yet they exhibited T_m values that did decrease with the freezing temperature, T_f. Water froze in one case at −0.6 °C, yet rapid freezing stopped at −3.9 and −7.1 °C in the other cases. To explain this behavior we must note that these pastes were nearly completely hydrated, and therefore the largest capillaries were *not* sufficiently numerous to permit ice formation up to a T_m characteristic of that size. In fact, Powers, Copeland, and Mann's study of paste permeability would indicate no interconnected capillaries in such fully hydrated pastes, whereas their work indicates that the specimens of figure 3 contained enough interconnected capillaries to affect strongly the permeability.

The same argument can be applied to the results obtained with the low water-cement ratio pastes shown in figure 6.

It is interesting to compare the initial freeze of the immature self-desiccated pastes in figure 9 with the similar water-soaked pastes of figure 7.

The T_m values of the pastes of figure 9 decreased steadily as the extent of hydration increased from 8 percent to 48 percent. The values were −0.6, −0.9, −1.3, −2.0, and −3.0 °C, the −2.0 °C occurring at 43 percent of the ultimate value of w_n/c, 0.230. In four of the water-soaked pastes of figure 7 expansions also began with T_m values of −2.0 °C; the extent of hydration ranged from 42 percent to 81 percent in these cases. These results indicate that up to about 42 percent of the ultimate value of w_n/c the largest capillaries of the self-desiccated pastes contain appreciable amounts of water which can be frozen, just as in the saturated pastes. It also indicates the existence of a network of large (−2 °C corresponds to 200 A diameter) capillaries, the sizes of which are not much dependent upon the extent of hydration, at least up to 81 percent of the ultimate w_n/c. However, the progressive reduction of the expansion indicates that this network of contiguous capillaries becomes less continuous as hydration proceeds.

Ice Formation Immediately Subsequent to the Initial Freeze

The results shown in figures 4, 5, 7, 8, and 9 show that the initial rapid formation of ice produces immediate expansions in pastes containing sufficient water. Though these expansions are not very large, immediately subsequent there are large progressive expansions which must be a result of the subsequent growth of the original dendrities.

Powers, Copeland, and Mann interpreted the reduction of paste permeability with hydration as resulting from the reduction of capillary continuity by filling of capillaries with products of cement hydration. The systematic reduction of the immediately subsequent expansions of the water-soaked paste as shown in figure 7 can be interpreted in the same way. The initial expansions began in each case at about −2 °C but were reduced to zero between the w_n/c values of 0.187 and 0.207 (81 to 90 percent of the cement hydrated).

The results presented in figure 9 are intrepreted to mean that freezing of water in these pastes began at about −1 °C, but only in specimens 55_2t, 52_1t, and 51_2b did the initial ice formation fill the spaces in which the freezing occurred. In the tests of the two other specimens, 55_1t and 55_1b, the freezing apparently did not occur in many water-filled capillaries until −2 and −3 °C respectively, because large expansions did not occur until these temperatures were reached, though continuing ice formation was evident at higher temperatures from the time-temperature curves in figures 10 and 11. Analysis of the variation of T_m with w_t/c and w_n/c for the self-desiccated specimens of figures 3 and 9 indicates that the temperatures at which the large expansions began in the tests of 55_1t and 55_1b are very nearly the T_m values that would have been observed if these specimens had not been seeded at higher temperatures. This result indicates that the large expansions began when it was cold enough for ice crystals to penetrate into many large water-filled capillaries, rather than by the filling up of partly empty capillary spaces by progressive freezing of the solution in these capillary spaces.

Progressive Extension of the Originally Formed Ice Network

The preceding discussion has been almost entirely concerned with the initially formed network of ice crystals in the capillaries of the paste. The effect of subsequent growth and thawing of this network is illustrated in the results shown in figures 12, 13, and 14. Additional ice formation was indicated by a progressive expansion at a temperature that depended on the capillary porosity as shown in figure 15. The additional expansion is believed to occur because a temperature is reached at which additional stable ice crystals can be formed in the smaller water-filled capillaries connected to those in which ice formed initially.

These specimens did not contain entrained air voids, but the specimen geometry provided escape boundaries with an equivalent void-spacing factor of 0.4 cm. Though this is too large to prevent destructive expansions it was small enough to reduce considerably the large progressive expansions of high water-cement ratio pastes. Specimens of such pastes without hollow cores yielded results similar to those with hollow cores but showed greater expansions. Nevertheless, these results show typical freezing-thawing hysteresis and permit calculation of the fraction of the capillary water which froze at the beginning of freezing. Neither of these aspects of the results is believed to be invalidated because of the moisture lost to the surface during freezing, though the magnitude of the expansion was affected by the loss.

Figure 15 shows a rapid decrease in the temperature of the progressive expansion between capillary porosities of 0.30 and 0.26. This decrease is no doubt partly a result of moisture movement from capillaries to gel during cooling. Such movement can have only little effect in pastes of high porosity because there is so much more capillary water in them than required to maintain the gel saturated during cooling. Even in pastes of low porosity the moisture redistribution with temperature does not seem to have a significant effect on the large progressive expansions at low temperatures because specimens TVt and SVb (of fig. 6) showed very similar freezing expansions beginning at about −18 °C, even though TVt had been stored in ice water before the test and SVb had not. Even more convincing are the results obtained with specimen 29_1b of figure 16. Though the capillary saturation coefficient of this paste was calculated to be only 0.82 at 23 °C, the large progressive expansion began at −19

°C, only 2 degrees C lower than that of the companion water-soaked specimen of figure 6, 9_1b. This result indicates that the temperature of the beginning of progressive freezing is more closely related to the pore structure of the paste than the saturation coefficient, though at very low porosities the effect of cooling on the capillary saturation coefficient must become very important.

Figure 15 indicates that even in pastes of relatively low porosities freezing resumed at about −17 °C. Table 1 indicates that at this temperature freezing could occur through capillaries of about 40 A diameter, which is not much greater than Powers' estimate of the average size of the gel pores in cement pastes from porosity and surface area considerations [31]. Since large freezing expansions occurred at this temperature in all water-saturated pastes tested, there must be a relatively large number of pores of this size in such pastes. It has also been shown that even pastes of low capillary porosity have some very large capillaries, those which permit a limited amount of ice formation near −1 °C. Capillaries of intermediate sizes were apparently not very numerous in these low water-cement ratio pastes. There seem to be two principal kinds of pores in these cement pastes, which Powers has called gel pores and capillaries. Figure 8 is a particularly good illustration of the effect of the binodal character of the pore-size distribution on freezing behavior during a single test.

The freezing-thawing hysteresis evident in figures 12, 13, and 14 is readily explained in terms of capillary size restrictions on ice formation. Water in many of the larger capillary spaces does not freeze until low temperatures are reached because they are not connected to the existing ice network through any capillaries large enough to contain stable ice crystals. Once they have become frozen at a lower temperature they will not melt until a temperature corresponding to the size of each particular frozen capillary is reached, and this temperature is apparently considerably higher than the temperature at which it became frozen. In actual experiments the freezing-thawing hysteresis curves are complicated by diffusion of water from unfrozen pores to ice in the frozen capillaries. The fact that expansions, supposedly resulting from this diffusion, can be observed is further evidence for the existence of certain pores in the paste in which the ice phase cannot be nucleated.

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Paper VI–S3. Comparison of Chemical Resistance of Supersulfate and Special Purpose Cements*

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Synopsis

Mortar specimens made with five supersulfate cements were exposed to solutions of various salts and acids, and their performance as judged by sonic measurements, weight loss, and appearance was compared with the performance of specimens made with portland blast-furnace slag, portland-pozzolan, sulfate-resistant, and high-alumina cements exposed to the same solutions. The testing solutions were prepared from magnesium sulfate, sodium sulfate, sugar, and lactic, sulfuric, citric, and acetic acids. A saturated solution of CO_2 in water was also used. Differences were observed in the resistance to attack of the various cementitious materials in the different solutions. The special-purpose cements appeared to resist attack as well as, and in some solutions better than, the supersulfate cements.

Résumé

Des spécimens de mortier faits avec cinq ciments sursulfatés furent exposés à des solutions de sels et d'acides variés, et leur comportement, apprécié par des essais soniques, la perte de poids, et l'aspect fut comparé au comportement des spécimens confectionnés avec un ciment portland au laitier de haut fourneau, un ciment portland-pouzzolanique, un ciment "sulfate-resistant" et un ciment alumineux, exposés aux mêmes solutions. Les solutions d'essais étaient préparées à partir de sulfate de magnésium, de sulfate de sodium, de sucre, et d'acides lactique, sulfurique, citrique et acétique. Une solution saturée de CO_2 dans l'eau fut également utilisée. On observa des différences dans la résistance à l'attaque des matériaux cimentaires variés dans les différentes solutions. Les ciments à but spécial semblèrent résister à l'attaque aussi bien, et dans certaines solutions certains étaient plus résistants que les ciments sursulfatés.

Zusammenfassung

Mörtelprobenkörper, die von fünf Sulfathüttenzementen hergestellt waren, wurden mit Lösungen verschiedener Salze und Säuren behandelt, und ihre Leistung, die durch Tönungmessungen, Gewichtsverlust und Aussehen bestimmt wurde, wurde mit der Leistung anderer Probenkörper, die aus Hochofenzement, Portlandpozzuolanzement, sulfatbeständigem Portlandzement und Tonerdezement hergestellt wurden, verglichen. Die Prüflösungen wurden aus Magnesiumsulfat, Natriumsulfat, Zucker, Milchsäure, Schwefelsäure, Zitronensäure und Essigsäure hergestellt. Eine gesättigte Lösung von CO_2 in Wasser wurde auch angewandet. Die verschiedenen Zementmaterialien zeigen verschiedenen Widerstand gegen den Angriff solcher Lösungen. Die Spezialzemente zeigten in vielen Fällen denselben Widerstand wie die Sulfathüttenzemente, und einige von diesen zeigten sogar einen besseren Widerstand in manchen Lösungen.

Introduction

There are a number of exposure conditions where concrete made with regular portland cement does not give satisfactory performance. Sea water, sulfate ground water, carbonated water, and water containing organic acids are detrimental to concrete. In dairies and wineries, either special coatings to protect the surface from attack, or special cements which offer greater resistance, are in use. Sulfate-resistant cement, pozzolanic cement, portland blast-furnace slag cement, high-alumina cement, and supersulfate cement are examples of the cements used. Various reports have been made relative to the use and durability of each of these types of cements, but no direct comparisons of all of them have been made. In order to make such comparisons, physical and chemical tests were made on a number of these cements. Since supersulfate cements are relatively unknown in the United States, although extensively used in Europe, several were included in order to obtain a range of properties of such cements. Mortar specimens made with the cements were exposed to solutions of various salts and acids, and the performance of the cements was judged by sonic measurements, weight loss, and change in appearance.

Materials

Five supersulfate cements were obtained for this study, four being commercial brands from Europe, and one an experimental cement produced in the United States. All possible precautions were taken to protect the cements during shipment. The cements used for comparison were a blend of 25 percent calcined shale and 75 percent Type I cement, a portland blast-furnace slag cement, a high-alumina cement, and a Type V sulfate-resistant cement. The chemical analyses are shown in table 1. The physical tests usually required in Federal and ASTM specifications for portland cement were also made; these test results are shown in table 2.

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Mortar specimens made of each of the above cements and graded Ottawa sand were exposed for chemical attack in solutions prepared from reagent or U.S.P.-grade chemicals. The following solutions were used:

magnesium sulfate	20g/l
sodium sulfate	20g/l
sugar solution	170g/l
lactic acid	45g/l
CO_2 solution, saturated	
sulfuric acid (Sp. Gr. 1.84)	10g/l
sulfuric acid (Sp. Gr. 1.84)	20g/l
citric acid	10g/l
acetic acid (glacial)	10g/l
saturated magnesium sulfate	------

The CO_2 solution was kept saturated by introducing a slow stream of CO_2 into the storage container from a tank of compressed CO_2 gas.

TABLE 1. *Chemical analyses*

(percents)

204, 206, 208, 210, 212 Supersulfate cements, 213 Portland-pozzolan cement, 214 Portland blast-furnace slag cement, 215 High-alumina cement, 216 Type V cement

Cement No.	204	206	208	210	212	213	214	215	216
Ignition loss	1.33	1.59	0.89	0.94	0.82	2.77	1.53	0.82	0.87
Insoluble residue	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	.14
SO_3	8.72	7.77	7.27	7.81	6.40	1.44	2.69	.20	1.75
MgO	5.78	5.92	3.83	3.63	4.45	1.85	3.31	1.10	.96
SiO_2	24.64	24.96	27.80	26.10	29.99	28.89	26.17	11.34	22.82
Al_2O_3	14.70	14.54	13.55	12.75	10.40	5.80	8.09	38.26	4.12
Fe_2O_3	(a)	(a)	(a)	(a)	(a)	4.06	2.13	6.69	4.14
CaO	41.80	42.02	43.60	45.92	46.27	54.10	54.92	35.25	64.22
Na_2O	.64	.68	.23	.26	.14	.30	.08	.09	(a)
K_2O	.42	.41	.81	.49	.48	.92	.20	.11	(a)
S	1.13	1.12	.88	.98	1.33	.004	.74	.21	(a)
Mn_2O_3	.92	1.03	.43	.90	.38	.00	.69	.00	(a)
FeO	.38	.41	.80	.49	.50	(a)	(a)	(a)	(a)
C_3S	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	49.5
C_3A	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	3.9

[a] Not determined.
[b] Not calculated.

TABLE 2. *Physical tests*

Cement No.	Normal consistency	Initial set	Final set	Specific gravity	Air entrainment	Air permeability fineness	Passing No. 325	Autoclave expansion	Compressive strength, 2-in. cubes						
									1 day	3 days	7 days	28 days	1 yr		
													Water storage	95 percent air [c]	50 percent air [d]
	Percent	*hr/min*	*hr/min*		*Percent*	*cm²/g*	*Percent*	*Percent*	*psi*	*psi*	*psi*	*psi*	*psi*	*psi*	*psi*
204	25.6	2:45	4:55	2.94	7.2	3,420	86.4	0.01	1,140	2,640	3,380	4,620	6,020	5,910	3,380
206	25.4	3:45	6:25	2.93	7.3	3,400	87.1	−.02	1,160	2,140	2,710	3,270	4,370	4,530	2,760
208	25.4	5:30	8:40	2.92	7.2	2,930	88.5	.06	700	2,590	4,370	6,420	7,980	8,350	4,780
210	23.0	5:15	8:15	2.97	7.0	4,030	93.7	−.00	1,100	3,070	6,510	8,430	10,220	10,390	8,540
212	(a)	1:55	4:40	2.95	5.8	6,750	99.8	.17	2,040	3,860	4,630	6,180	7,980	8,280	6,600
213	29.6	3:10	5:35	3.05	8.3	4,690	90.6	.11	840	2,120	3,330	5,740	7,380	7,420	5,620
214	27.4	4:05	6:15	3.03	8.2	3,980	98.7	.02	1,330	2,410	3,750	7,160	8,460	8,320	6,630
215	24.4	(b)	(b)	3.11	6.8	2,930	80.9	−.04	4,660	5,430	5,620	6,130	6,170	6,020	5,990
216	24.2	4:25	6.10	3.18	(e)	3,040	98.8	.01	990	2,040	3,250	5,070	6,440	7,670	5,470

[a] Could not obtain normal consistency, as the cement had a tendency to flash set.
[b] Did not reach initial set in 10 hr.
[c] One yr in moist cabinet, air at 95 percent rh, never in water.
[d] Six days in water, 49 wk laboratory air at 50 percent rh, then 2 wk in water.
[e] Not obtained.

Test Procedure

Test specimens were 40 x 40 x 160-mm prisms made with one part of cement and 2.75 parts of graded Ottawa silica sand in accordance with Method 2701 (May 1, 1957) of Federal Test Method Standard No. 158. The specimens were removed from the molds after 24 hr in the moist cabinet, then stored in water for 6 days. Control specimens remained in water storage thereafter. Three test specimens of each of the nine cements were made on the same day for storage in one of the solutions. Since exposure to air during setting causes a friable, dusty surface layer on specimens containing supersulfate cements, molds containing these specimens were placed in the moist cabinet in plastic bags, reducing the friable layer to a thin film. At 7 days, the specimens were weighed, and the fundamental transverse frequency determined (Method 4101 of Federal Test Method Standard No. 158). Specimens were than placed in glass jars, supported so that all sides were exposed, and covered with approximately 6 liters of solution; there was no agitation of the solutions during the test period.

Measurements of frequency and weight were made at 14, 21, and 28 days after the specimens were fabricated and each 28 days thereafter, and the appearance of the specimens was recorded at each measurement. The test specimens were placed in a fresh solution after each of these intervals. The acid solutions were probably neutralized before the end of each exposure period, so that the number of cycles of attack is more important than the age of the specimens. Specimens made with all nine cements were stored in the same jar of solution except the acetic acid, where an excessive black sediment from the high-alumina cement coated all the other specimens and obscured the identification number. Consequently these specimens were stored separately.

For the specimens exposed to saturated magnesium sulfate solution, a different schedule was adopted. Each 7 days a 3-day soaking period was followed by a 4-day drying period in laboratory air at approximately 73 °F. and 50 percent rh, measurements being made after drying. After the specimens were 28 days old, the soaking and drying periods were continued, but measurements were made only at 28-day intervals.

Test Results

The test results, in the form of average frequency measurements are recorded in table 3 which also shows the final average weight changes. Part of the test results are also portrayed in figure 1, which shows the relationship between fundamental frequency and cycles of exposure for the specimens in some of the solutions, as well as the frequency of control specimens at various ages.

Figure 2 shows the condition of the specimens at the end of the test in citric acid, sulfuric acid (20g/l), and saturated magnesium sulfate solutions. The following solutions appeared to have relatively minor effects on the specimens: sodium sulfate, magnesium sulfate (10g/l), sugar, and saturated CO_2 solution. Specimens containing the four commercial supersulfate cements showed minor loss of material from the corners and edges in the magnesium sulfate solution and slight surface pitting in the sugar solution. Increases in weight were not significant, and were generally less than the increase in weight of corresponding control specimens. The rate of increase of strength, as indicated by the fundamental frequency, was slower for specimens stored in the sugar solution than for the control specimens, those containing calcined shale indicating very little increase after 28 days, although the control specimens gained rapidly. In the sodium sulfate solution, specimens made with portland blast-furnace slag, portland-pozzolan, and Type V cements had higher rates of increase than the control specimens for the first four months, then leveled off at higher frequencies than the controls.

The specimens stored in sulfuric acid (10g/l) appeared to resist attack for four to six cycles, then showed progressive loss of strength. The high-alumina-cement specimens were badly eroded on the corners, edges, and faces and lost weight, although coated with sulfates. All of the other specimens increased slightly in weight due to sulfate deposits, although there was some loss of material from the edges and corners.

Lactic acid, acetic acid, citric acid, and sulfuric acid (20g/l) caused immediate and severe loss of strength in all specimens containing supersulfate and high-alumina cements. Specimens made with portland blast-furnace slag, portland-pozzolan and Type V cements showed a normal rate of increase of frequency for three cycles of exposure to citric acid and sulfuric acid (20g/l), then deteriorated slowly. In the lactic acid solu-

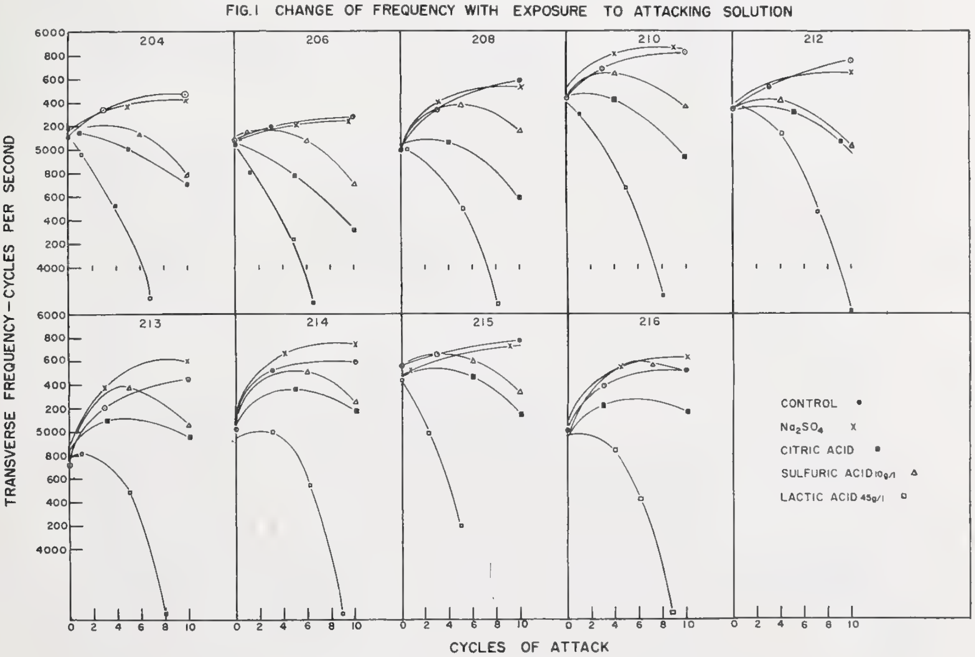

FIGURE 1. *Change of frequency with exposure to attacking solution.*

TABLE 3. *Transverse frequency of specimens stored in—*

Cycles per second

Cement No.	Age, days											Wt. change[a] g
	Initial	14	21	28	56	84	112	140	168	196	224	
						$MgSO_4$ (20 g/l)						
204	5, 070	5, 150	5, 180	5, 190	5, 200	5, 210	5, 200	5, 200	5, 210	5, 210	5, 200	+3
206	5, 050	5, 100	5, 150	5, 150	5, 190	5, 230	5, 230	5, 210	5, 200	5, 220	5, 210	+3
208	4, 980	5, 250	5, 320	5, 350	5, 440	5, 460	5, 490	5, 490	5, 490	5, 490	5, 480	+4
210	5, 400	5, 600	5, 640	5, 660	5, 710	5, 720	5, 720	5, 730	5, 720	5, 710	5, 700	+2
212	5, 390	5, 480	5, 500	5, 520	5, 580	5, 620	5, 640	5, 660	5, 660	5, 680	5, 690	+5
213	4, 740	5, 150	5, 260	5, 330	5, 450	5, 520	5, 510	5, 520	5, 520	5, 540	5, 550	+7
214	5, 020	5, 430	5, 530	5, 580	5, 680	5, 720	5, 730	5, 750	5, 750	5, 750	5, 750	+8
215	5, 430	5, 570	5, 640	5, 680	5, 740	5, 830	5, 840	5, 890	5, 900	5, 910	5, 910	+6
216	4, 930	5, 290	5, 420	5, 480	5, 580	5, 650	5, 660	5, 690	5, 690	5, 700	5, 700	+6
						(Na_2SO_4 (20 g/l)						
204	5, 130	5, 250	5, 280	5, 300	5, 350	5, 360	5, 400	5, 430	5, 430	5, 430	5, 440	+3
206	5, 050	5, 110	5, 130	5, 130	5, 200	5, 200	5, 220	5, 240	5, 250	5, 260	5, 270	+3
208	4, 980	5, 210	5, 300	5, 330	5, 430	5, 470	5, 500	5, 510	5, 540	5, 540	5, 540	+3
210	5, 500	5, 650	5, 700	5, 740	5, 800	5, 820	5, 840	5, 850	5, 870	5, 870	5, 860	+3
212	5, 370	5, 440	5, 510	5, 510	5, 570	5, 590	5, 600	5, 620	5, 650	5, 650	5, 650	+3
213	4, 830	5, 170	5, 290	5, 360	5, 490	5, 560	5, 560	5, 600	5, 600	5, 610	5, 600	+6
214	5, 010	5, 400	5, 480	5, 590	5, 680	5, 730	5, 750	5, 750	5, 750	5, 750	5, 760	+5
215	5, 480	5, 510	5, 530	5, 560	5, 610	5, 650	5, 670	5, 690	5, 720	5, 720	5, 730	+5
216	4, 970	5, 310	5, 420	5, 470	5, 610	5, 660	5, 670	5, 700	5, 700	5, 710	5, 730	+9
						Sugar Solution (170 g/l)						
204	5, 110	5, 210	5, 230	5, 250	5, 290	5, 280	5, 310	5, 310	5, 320	5, 300	5, 270	−0
206	5, 050	5, 110	5, 140	5, 150	5, 170	5, 170	5, 180	5, 180	5, 180	5, 150	5, 110	−2
208	4, 980	5, 180	5, 220	5, 230	5, 300	5, 320	5, 330	5, 340	5, 340	5, 340	5, 300	−8
210	5, 430	5, 520	5, 540	5, 570	5, 610	5, 620	5, 640	5, 640	5, 640	5, 650	5, 630	−6
212	5, 350	5, 450	5, 450	5, 490	5, 560	5, 570	5, 610	5, 640	5, 630	5, 630	5, 630	+4
213	4, 770	5, 000	5, 040	5, 100	5, 190	5, 140	5, 120	5, 130	5, 160	5, 150	5, 140	+7
214	5, 010	5, 270	5, 340	5, 400	5, 470	5, 470	5, 470	5, 500	5, 510	5, 520	5, 520	+5
215	5, 530	5, 550	5, 550	5, 560	5, 580	5, 580	5, 580	5, 600	5, 610	5, 620	5, 650	+5
216	5, 000	5, 170	5, 210	5, 250	5, 270	5, 270	5, 270	5, 300	5, 300	5, 310	5, 340	+3
						Lactic Acid (45 g/l)						
204	5, 140	4, 960	4, 810	4, 800	4, 520	4, 340	3, 860	3, 600	3, 320	3, 040	2, 740	−38
206	5, 030	4, 800	4, 660	4, 650	4, 400	4, 240	3, 820	3, 560	3, 310	3, 050	2, 780	−37
208	5, 010	4, 940	4, 860	4, 850	4, 630	4, 500	4, 200	3, 940	3, 670	3, 380	3, 100	−36
210	5, 400	5, 290	5, 160	5, 160	4, 860	4, 660	4, 320	4, 030	3, 730	3, 410	3, 100	−35
212	5, 380	5, 310	5, 220	5, 220	5, 120	5, 000	4, 730	4, 460	4, 100	3, 930	3, 620	−23
213	4, 730	4, 820	4, 680	4, 730	4, 610	4, 390	4, 060	3, 720	3, 370	3, 050	2, 730	−29
214	4, 960	5, 000	4, 950	5, 000	4, 960	4, 780	4, 530	4, 160	3, 760	3, 340	---------	−28
215	5, 450	5, 220	4, 990	5, 070	4, 540	4, 180	---------	---------	---------	---------	---------	−81
216	4, 950	4, 980	4, 870	4, 920	4, 830	4, 670	4, 430	4, 060	3, 700	3, 310	---------	−34
						CO_2 Saturated						
204	5, 110	5, 100	5, 150	5, 150	5, 170	5, 180	5, 200	5, 200	5, 200	5, 220	5, 160	+2
206	5, 070	5, 010	5, 050	5, 050	5, 080	5, 080	5, 100	5, 100	5, 100	5, 090	5, 030	0
208	5, 000	5, 040	5, 110	5, 140	5, 210	5, 230	5, 240	5, 260	5, 270	5, 260	5, 210	0
210	5, 400	5, 490	5, 540	5, 580	5, 620	5, 640	5, 660	5, 670	5, 680	5, 680	5, 680	0
212	5, 360	5, 410	5, 460	5, 470	5, 490	5, 500	5, 500	5, 520	5, 510	5, 510	5, 460	+1
213	4, 730	4, 970	5, 060	5, 140	5, 280	5, 280	5, 300	5, 280	5, 280	5, 270	5, 230	+1
214	4, 990	5, 290	5, 410	5, 450	5, 540	5, 540	5, 540	5, 530	5, 530	5, 530	5, 480	+1
215	5, 430	5, 470	5, 540	5, 590	5, 690	5, 720	5, 760	5, 770	5, 780	5, 790	5, 800	+4
216	4, 960	5, 210	5, 320	5, 380	5, 480	5, 490	5, 500	5, 490	5, 490	5, 480	5, 430	+1
						H_2SO_4 (10 g/l)						
204	5, 100	5, 180	5, 170	5, 190	5, 200	5, 160	5, 160	5, 050	4, 970	4, 870	4, 790	+4
206	5, 090	5, 150	5, 150	5, 170	5, 170	5, 120	5, 000	5, 000	4, 930	4, 830	4, 720	+6
208	5, 000	5, 260	5, 320	5, 360	5, 410	5, 360	5, 350	5, 320	5, 280	5, 240	5, 160	+7
210	5, 410	5, 580	5, 580	5, 620	5, 630	5, 590	5, 570	5, 540	5, 470	5, 440	5, 360	+8
212	5, 340	5, 400	5, 390	5, 440	5, 410	5, 360	5, 320	5, 270	5, 170	5, 110	5, 040	+24
213	4, 780	5, 130	5, 220	5, 330	5, 400	5, 380	5, 350	5, 300	5, 200	5, 150	5, 060	+24
214	4, 960	5, 300	5, 430	5, 500	5, 570	5, 550	5, 530	5, 470	5, 410	5, 340	5, 270	+21
215	5, 550	5, 620	5, 620	5, 660	5, 680	5, 650	5, 610	5, 600	5, 340	5, 400	5, 320	−22
216	4, 960	5, 290	5, 380	5, 430	5, 560	5, 590	5, 600	5, 580	5, 550	5, 550	5, 500	+13

[a] Change in weight at 224 days, or at last age for which frequency is shown.

TABLE 3. *Transverse frequency of specimens stored in*—Continued

Cycles per second

Cement No.	Age, days											Wt. change[a] g
	Initial	14	21	28	56	84	112	140	168	196	224	
						H_2SO_4 (20 gl/)						
204	5, 150	5, 100	4, 970	4, 990	4, 900	4, 870	4, 720	4, 620	4, 470	4, 270	----------	+14
206	5, 110	5, 040	4, 910	4, 930	4, 800	4, 690	4, 540	4, 370	4, 170	3, 960	----------	+20
208	5, 053	5, 200	5, 160	5, 190	5, 060	4, 950	4, 820	4, 650	4, 460	4, 260	----------	+21
210 [b]	5, 470	5, 530	5, 340	5, 330	4, 950	[b] 5, 250	5, 000	4, 800	4, 420	----------	----------	−60
212 [b]	5, 380	5, 300	5, 010	5, 000	3, 630	[b] 5, 030	4, 660	4, 550	4, 290	----------	----------	−99
213	4, 830	5, 060	5, 180	5, 260	5, 200	5, 030	4, 900	4, 740	4, 550	----------	----------	−45
214	4, 990	5, 280	5, 360	5, 440	5, 330	5, 160	4, 990	4, 930	4, 750	4, 530	----------	−10
215	5, 520	5, 530	5, 340	5, 350	5, 140	4, 890	4, 650	4, 450	4, 220	4, 060	----------	−11
216	4, 980	5, 320	5, 310	5, 390	5, 410	5, 360	5, 230	5, 120	5, 020	4, 800	----------	−214
						Citric Acid (10 g/l)						
204	5, 170	5, 130	5, 040	5, 040	5, 050	5, 010	4, 950	4, 860	4, 820	4, 780	4, 700	−13
206	5, 110	5, 000	4, 920	4, 890	4, 880	4, 780	4, 680	4, 580	4, 490	4, 420	4, 320	−15
208	5, 040	5, 110	5, 060	5, 060	5, 090	4, 980	4, 930	4, 840	4, 750	4, 690	4, 590	−16
210	5, 430	5, 500	5, 430	5, 430	5, 430	5, 350	5, 260	5, 180	5, 100	5, 040	4, 950	− 16
212	5, 310	5, 390	5. 320	5, 330	5, 360	5, 320	5, 250	5, 170	5, 110	5, 060	5, 990	−14
213	4, 790	4, 990	5, 020	5, 080	5, 170	5, 080	5, 080	5, 060	5, 030	5, 020	4, 950	−105
214	4, 990	5, 220	5, 270	5, 320	5, 370	5, 350	5, 350	5, 240	5, 220	5, 220	5, 200	−60
215	5, 470	5, 510	5, 400	5, 480	5, 550	5, 520	5, 450	5, 390	5, 300	5, 230	5, 130	−45
216	4, 920	5, 140	5, 190	5, 220	5, 290	5, 300	5, 250	5, 220	5, 210	5, 090	5, 170	−50

[a] Change in weight at 224 days, or at last age for which frequency is shown.

[b] Soft surface peeled off leaving hard surface.

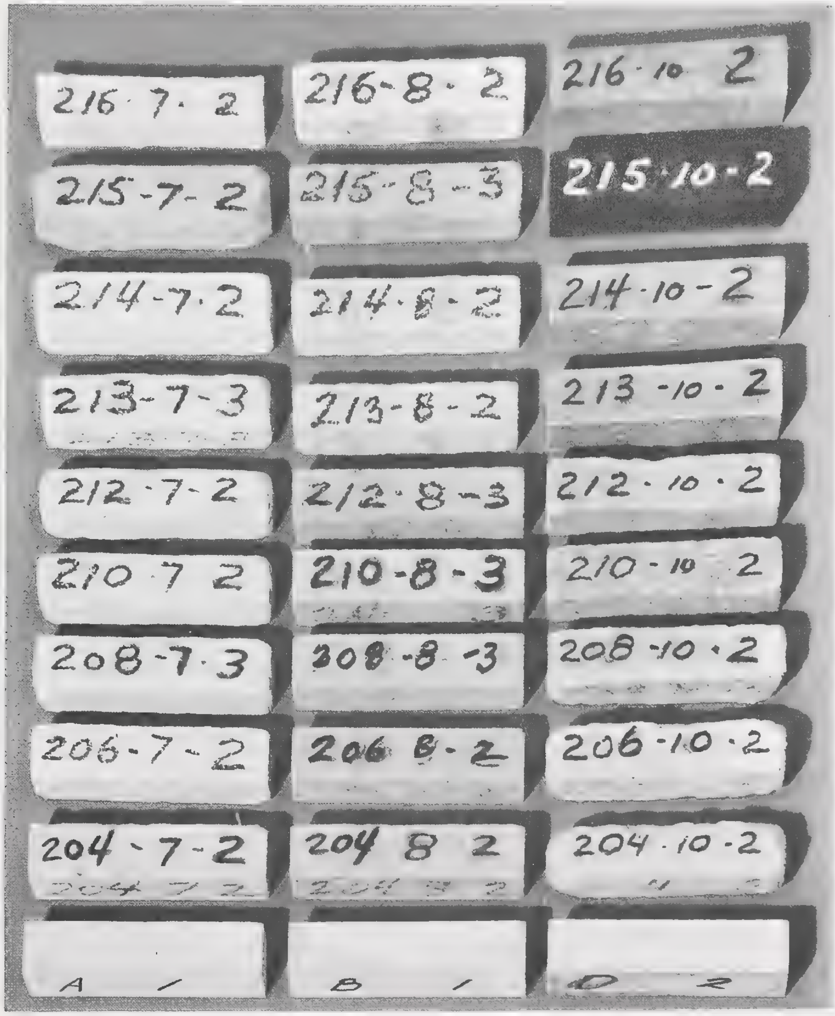

FIGURE 2. *Appearance of mortar specimens after exposure to:* (*7*) H_2SO_4, *20 g/l,* (*8*) *citric acid,* (*10*) $MgSO_4$, *wetting and drying.*

tion, the high-alumina-cement specimens were so badly eroded that they were removed after six cycles, but the other specimens showed only slight surface granulation accompanied by a considerable weight loss due to leaching. Specimens stored in acetic acid lost some weight, but showed no surface damage except surface granulation of specimens containing high-alumina cement. The citric acid caused moderate weight loss from all specimens, moderate coatings of calcium citrate on specimens made with supersulfate cements, and heavy coatings for the other specimens, except those containing high-alumina cement, which were not coated, but had a soft, spongy surface.

In the sulfuric acid solution (20g/l), specimens containing three of the supersulfate cements increased slightly in weight and were not eroded but the soft surfaces and the decrease in frequency indicated extensive loss of strength. The other specimens exhibited weight loss and surface damage. Spongy surface coatings made determination of the fundamental frequencies difficult. However, when the surface coatings were removed, clear patterns were obtained on the oscilloscope which indicated that the damage was limited to the exposed surface.

The frequency is dependent on the size of a specimen as well as the weight, strength, and shape. For most of the specimens and for most solutions, changes in size were so small that they could be disregarded. There were appreciable changes in the dimensions of the special cements in citric acid, and sulfuric acid (20g/l), and as smaller specimens should have higher frequencies, these specimens deteriorated more rapidly than indicated by the frequency change. Supersulfate cements in these solutions remained about the same dimensions, but became soft and granular.

In saturated magnesium sulfate solution with alternate wetting and drying, specimens containing three of the supersulfate cements deteriorated so rapidly that they had to be removed after three cycles. The other specimens showed a slight increase in frequency, those containing the high-alumina cement being closest to the control specimens. There was some pitting of the surfaces of specimens made with the other two supersulfate cements, and all specimens except those containing the high-alumina cement showed some loss in weight.

Discussion

In part because their resistance is superior to that of regular portland cement, supersulfate cements are used in situations where concretes are exposed to sulfate waters and where they are in contact with gypsum deposits. The principal constituents of these cements are blast-furnace slag, portland cement, and enough gypsum for a SO_3 content of 7 to 9 percent. The reaction of the granulated slag with water to form a hardened mass is slow unless accelerated by a small amount of lime, which is usually obtained from portland-cement clinker added to the cement in manufacture. The calcium sulfate also acts as an accelerator, as in portland cement when added in excess of the amount needed to retard the setting. Due to the low concentration of CaO and the high concentration of SO_4, the high form of calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is formed in supersulfate cement, to which the cement owes part of its strength and superior resistance [1].[1] In this form the alumina is not available to react with sulfate waters with resulting distress to the concrete. In portland cement the low form of calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) is formed during hardening, which can then further react with sulfate solutions.

In addition, supersulfate cement does not form large amounts of $Ca(OH)_2$ during hardening, as does portland cement by hydrolysis of di- and tricalcium silicate. Thus one of the claimed advantages for supersulfate cement [2] is that there is no $Ca(OH)_2$ free in the hardened concrete and available for leaching, with consequent increase of porosity of the concrete. However, it has not been proved [3] that leaching of the $Ca(OH)_2$ formed in hydrated portland cement is a factor in the sulfate attack of concrete, since cements of high tricalcium-silicate content may be sulfate-resistant if the tricalcium-aluminate content is low.

The hydrous calcium silicates of portland cement, approximately of the composition $3CaO \cdot 2SiO_2 \cdot nH_2O$, are relatively insoluble in comparison with sulfates and sulfoaluminates. The presence of the latter in hardened concrete would permit increased penetration and more rapid attack by acid solutions than would the calcium silicates in portland cement concrete. This factor may be responsible in part for the observed lower resistance of supersulfate cements to acid solutions.

Summary and Conclusions

Specimens of all of the cements tested showed good resistance to sodium sulfate, CO_2, and sugar solutions, except that the supersulfate cements underwent surface pitting in the sugar solution. Supersulfate cements did not resist the attack of magnesium sulfate solutions as well as did the other cements. In some of the acid solutions, particularly acetic and sulfuric (10g/l), the specimens of supersulfate cements remained the same size and showed only a slight loss of weight in the saturated condition. However the rapid decrease in frequency and the formation of a soft, granular surface indicated extensive damage to the internal structure of the mortar specimens. The high-alumina cement showed relatively poor resistance to lactic and sulfuric acid solutions. It is concluded that although the supersulfate cements offer excellent resistance to attack by sodium and calcium sulfates, they do not equal the resistance of the special-purpose cements to attack by magnesium sulfate and some of the acid solutions.

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[1] Figures in brackets indicate the literature references at the end of this paper.

References

[1] Léon Blondiau and Yvan Blondiau, Action du sulfate de calcium sur la prise des ciments métallurgiques sursulfatés et des ciments de haut fourneau. Revu. des matériaux construct. et trav. publ., No. 453, p. 165.

[2] Léon Blondiau, Les ciments métallurgiques sursulfatés et applications dans les travaux exposés aux agents agressifs. Quatorzième Congrès de Chimie Industrielle, Paris, October 21–27, 1934, p. 14.

[3] F. R. McMillan, T. E. Stanton, I. L. Tyler, and W. C. Hansen, Long-time study of cement performance in concrete. Chapter 5, Concrete exposed to sulfate soils, Special Publication of the Am. Concrete Inst. 1949; Research Labs., Portland Cement Assoc. Bull. No. 30.

Discussion

T. D. Robson

The testing of different cement mortars in even the most highly concentrated sulfate solutions is obviously justified as a practical procedure, since such concentrations can often be encountered by concretes under service conditions.

On the other hand, no hydraulic cement is claimed to be proof against moderately strong solutions of acids, and consequently there seems little point in testing the various cements at acid concentrations much stronger than those for which any of the cements could be recommended in practice.

Recommended acidity limits are usually about pH 4.0 for high-alumina cements and pH 3.0 to 3.5 for supersulfated cements (although concretes made with the latter cements can give good service in sulfuric acid of pH slightly below 1.0). Claims made for the superior acid resistance of both these types of cement apply only within some limits such as the above (which cover a wide range of industrial effluents, products of combustion, acid grounds, etc.). Once the restricted limits of acidity are grossly exceeded, all hydraulic cements are attacked to a degree which normally precludes their continued use, and a comparison of their resistance to stronger acids is rendered more irrelevant by the fact that the relative "order of merit" can change more than once with increasing acid concentration.

When specimens made from different types of cement are all immersed together in sulfate solution, there is always the possibility of secondary reactions which can, in effect, alter the test conditions to the detriment of one or more of the cements. In the investigation under discussion there is no indication of any such complication but the storage of different-type specimens in a common solution should probably be avoided.

Discussion

E. Burke

Tests on supersulfated cement have been carried out in our laboratories over the last 8 yr and the author's results can be confirmed where they overlap. This is particularly the case with solutions of magnesium sulfate in which its performance was inferior to that of sulfate-resisting portland cement of the type used by the authors. It was found that up to about 3 or 4 yr the supersulfated cement was apparently superior but that it deteriorated rapidly beyond this age (fig. 1). A similar effect was noticed in triple-strength sea water (fig. 2). It should be noted, however, that our tests were made on standard concretes totally immersed in the solutions, which were renewed at monthly intervals, as against the mortar specimens used by the authors. Quality of the concrete was judged by compressive strength tests.

In the case of sodium sulfate solutions no significant difference was observed in the resistance of concrete made with these two types of cement at 8 yr but the strength of the supersulfated cement was decreasing rapidly whereas the type V was steady (fig. 3).

For sulfuric acid solutions of 0.5 percent or greater strengths no difference was found in the resistance of concretes made with Type I, Type V, aluminous cement, or supersulfated cement. They all deteriorated rapidly. In these cases the solutions were maintained at full strength as it was found that, especially at early periods, the solutions were rapidly neutralized. It was found that if the solutions were not maintained in strength false results were obtained and it is suspected that some of the published results on the resistance of cements to acids suffer from this error.

There is a possibility that supersulfated cement has a superior resistance to weak acid solutions in the range of pH 2.5 and upwards. There is, however, a marked lack of experimental data in this range and it would be useful if the gap in our knowledge could be filled.

In the past, several workers have placed reliance on the expansion of mortar bars in sulfate solutions to show their resistance to attack. Although this can be quite a useful indication in the case of cements of the portland type, it is not of any value for supersulfated cements which can break up and disintegrate without any appreciable longitudinal expansion. This was pointed out by Dr. Lea some years ago.[1] We have found that the only really

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[1] F. M. Lea, The Chemistry of Cement and Concrete, pp. 302, 541 (1956).

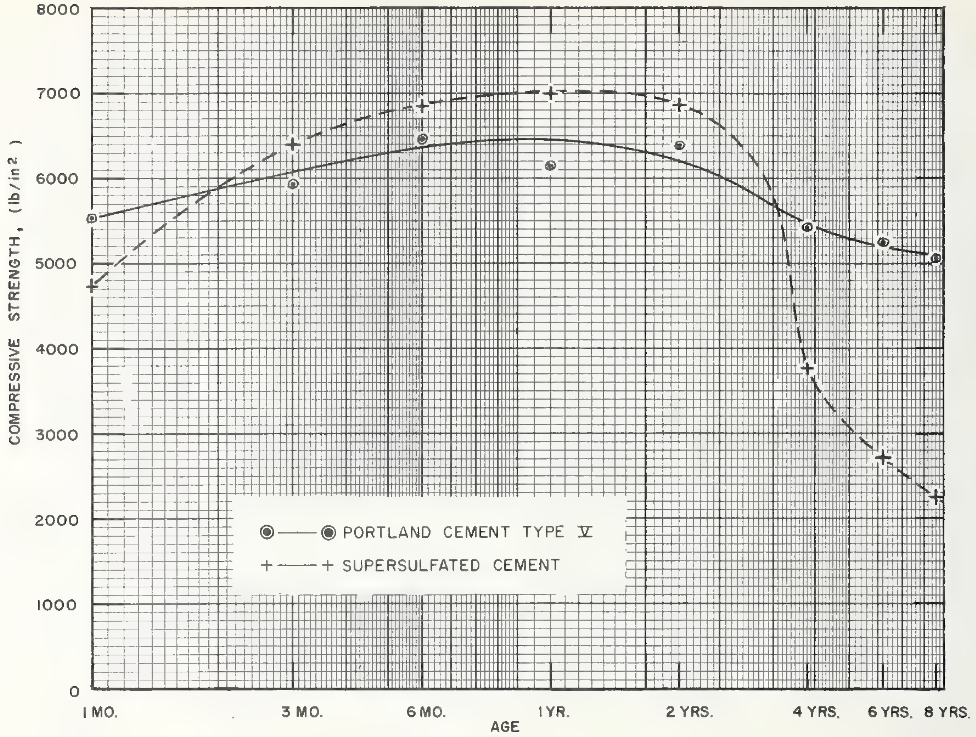

FIGURE 1. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in $MgSO_4$ solution (1.0% SO_4) after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

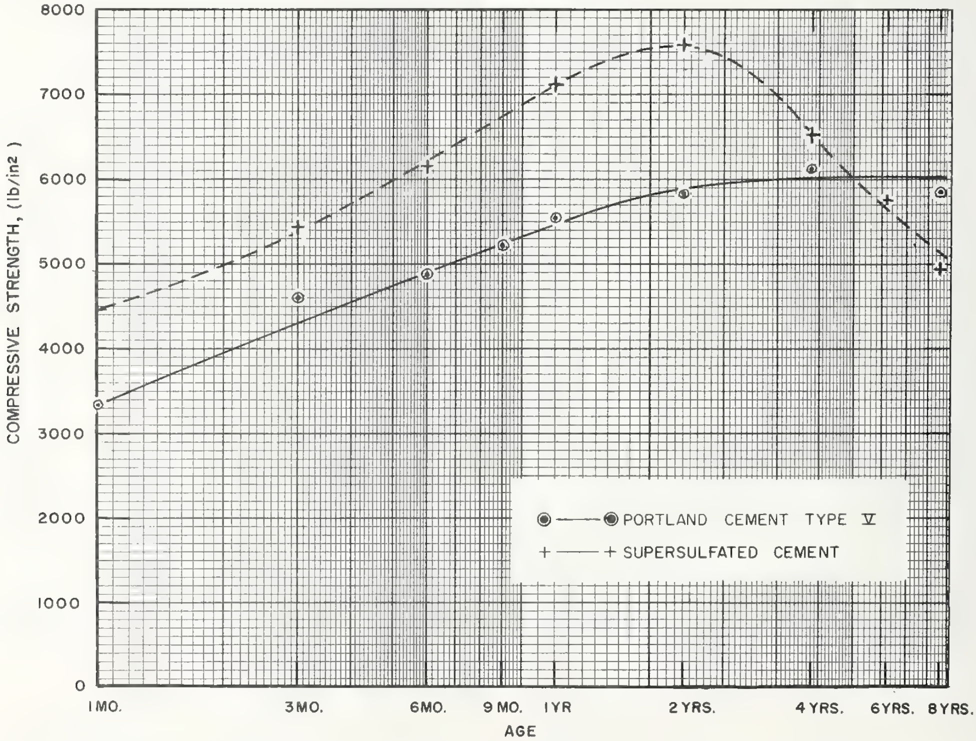

FIGURE 2. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in triple-strength sea water after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

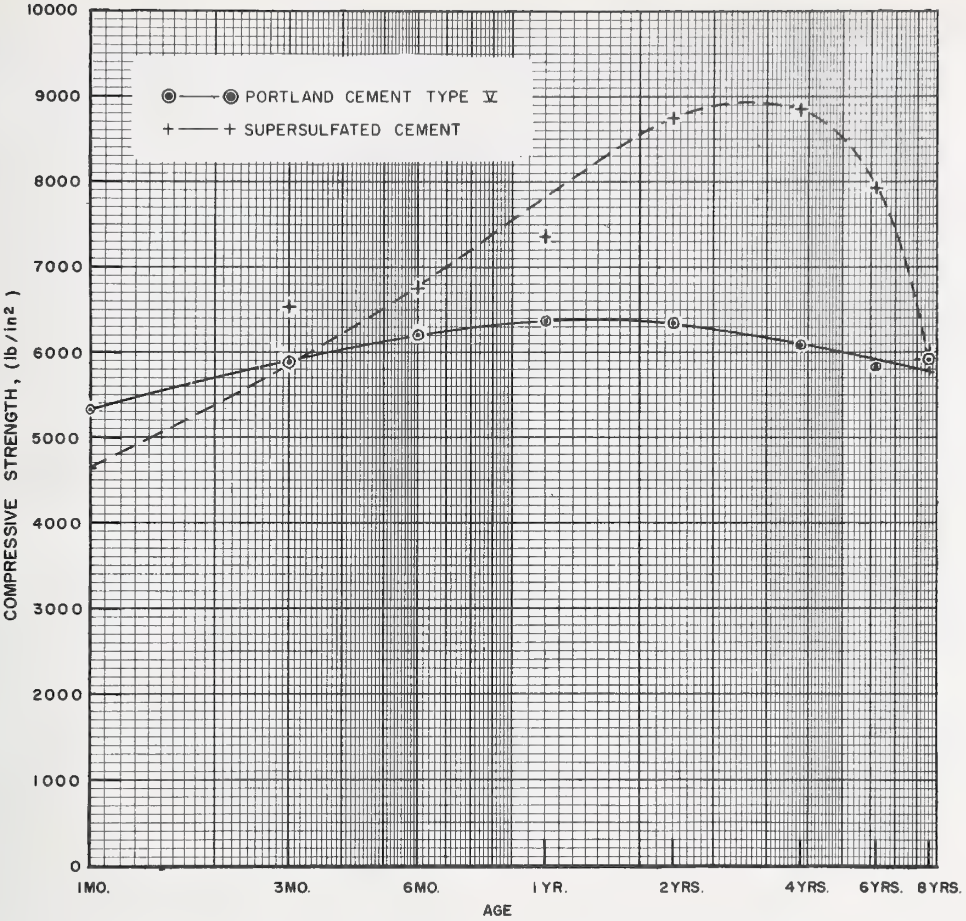

FIGURE 3. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in $NaSO_4$ solution (1.0% SO_4) after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

reliable test, particularly when comparing different types of cement, is one that uses the compressive strength to judge the quality of the concrete.

The resistance of sulfate-resisting portland cement to magnesium sulfate solutions is surprising. One would expect that the presence of magnesium would lead to a much greater rate of attack than is the case. It is possible that the formation of magnesium hydroxide fills the capillaries in the mass, thus increasing the resistance to penetration of the aggressive solution.

Universal experience has shown that the greatest safeguard against aggressive attack is a dense concrete. A further safeguard is a resistant cement, particularly in the more aggressive solutions. In this connection I feel that the application of Powers' work will be of the very greatest importance and it is likely that the solution to many of the problems of aggressive attack will be found in his paper to this Symposium.

Discussion

Julie Chi-Sun Yang

In this discussion, I would like to describe some observations on the chemical resistance of supersulfated slag cement which resulted from our work at Johns-Manville Research Center on these cements.

Supersulfated slag cements are widely known for their chemical stability in aggressive media, especially sulfate-bearing environments. When these slag cements are hydrated at room temperature, ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is found to be the main contributor to the strength and the chemical resistance, as Messrs. Evans, Blaine, and Worksman indicated. However, it was found that ettringite was not stable in dilute acid solutions; it decomposed to form gypsum in large quantities, and great volume expansion accompanied the decomposition.

In the paper presented by Mr. Evans and others, the authors mentioned that all the specimens used for chemical resistance tests were cured in the moist cabinet for 24 hr and then were stored in water for 6 days, presumably at room temperature.

Up to the present time, our knowledge of the hydration of slag cement at elevated temperatures and pressures is not as far advanced as that which we have of portland cement. It is believed that the chemical stability of supersulfated slag cement can be further improved with regard to the action of dilute mineral acids and organic acids when the setting of the slag cement structures is controlled carefully. Following an initial setting period at room temperature, the process of autoclaving at elevated temperatures and pressures is recommended.

We found that these supersulfated slag cement structures, cured at room temperature under water or at highly humid conditions for a few hours to about one day and then autoclaved under saturated steam pressure up to 200 psi for 8 to 24 hr, have desirable chemical resistance.

Two commercially available supersulfated slag cements purchased from European countries were investigated (Frodingham cement from England and Sealithor cement from Belgium). They both consist of about: 89–90 percent glassy slag, 7–15 percent calcium sulfate as anhydrite, and up to 5 percent alkali activator. The major components are:

SiO_2	25 to 30 percent
Al_2O_3	11 to 15 percent
CaO	40 to 45 percent
MgO	up to 5 percent
SO_3	approximately 6 to 9 percent

From X-ray diffraction patterns and microscopic examinations, it was found that all the ettringite contributing to the early strength is decomposed, and from this, anhydrite, $CaSO_4$ forms. In the absence of silica, the remaining amorphous lime and alumina probably will interreact to form calcium aluminate hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$. However, with the available silica from the disintegration process of the glass slag which is in a highly reactive form, hydrogarnet-like phases are formed with hydrated calcium silicates and calcium aluminates.

Hydrogarnets such as $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ and their solid solution series, including the corresponding partially iron-substituted compounds, are identified by their characteristic X-ray diffraction patterns.

Members of the hydrogarnet series are generally unreactive to sulfate solutions; our laboratory results also indicate that they are chemically stable to organic acids and dilute mineral acids. The details of the stability study of the hydrogarnets will be published in a separate paper.

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Paper VI–S4. Chemical Resistivities of Various Types of Cements*

Renichi Kondo

Synopsis

The chemical resistivity of cement should be very important especially in Japan, where there is a long coastline and consequently the concrete structures are frequently in contact with sea water. The chemical attack by 2 percent $MgSO_4$ solution on various types of cement mortar, where the cement sand ratio was 1:4, was examined with results as follows:

1. Sufficient durabilities were obtained with alumina cement, sulfate-resistant, and low-heat portland cements.
2. The durabilities of portland blast-furnace cement and portland silica cement were not always as high as those of normal and high-early-strength portland cements; therefore, special care should be taken in manufacturing the former two.
3. The durability of each portland, portland blast-furnace, and portland silica cement might be raised by increasing the addition of calcium sulfate nearly up to 2–4 percent as SO_3.
4. In the specimens containing portland blast-furnace cement, the external portion was severely cracked because of excessive expansion, while the internal part was intact, more stable than in the case of portland cement.
5. In the altered external layer, many needle-shaped gypsum crystals were found with ettringite.
6. In order to improve the resistivity of portland blast-furnace cement, it seemed desirable either to raise the amount of gypsum regardless of its modification, or to increase the slag content up to about 60 percent, or to grind the slag more coarsely than normal cement especially when the former was contained only to the extent of about 30 percent.
7. Though the external part of the specimens containing sulfated slag cement was finely cracked, the internal part remained entirely unattacked.

Next, the resistivity of hardened cement against neutralization is important, especially with the sulfated slag cement, because neutralization causes not only the risk of rusting of the reinforcing steel but also the reduction of bending strength and surface hardness.

These facts seemed to be related to the decomposition of ettringite by carbonic acid gas in air, with liberation of gypsum. The neutralization could be prevented by coating the surface thinly with water glass.

Résumé

Il faut souligner l'importance de la résistivité chimique du ciment spécialement au Japon où la ligne côtière est si longue et où les constructions en béton se trouvent par conséquent très souvent au contact de l'eau de mer. On a examiné l'attaque chimique d'une solution à 2% de $MgSO_4$ sur différentes sortes de mortier de ciment où le rapport ciment: sable était 1:4. Les résultats sont les suivants:

1. Des durabilités suffisantes furent obtenues avec le ciment alumineux, le ciment portland résistant aux sulfates et le ciment portland à faible échauffement.
2. Les durabilités du ciment portland au laitier de haut fourneau et du ciment portland-silice n'étaient pas toujours aussi hautes que celles des ciments portland normaux et à haute résistance initiale; par conséquent la fabrication des deux premiers devraient faire l'objet d'un soin particulier.
3. La durabilité du ciment portland, du ciment portland au laitier de haut fourneau, et du ciment portland-silice pourrait être élevée par l'addition accrue de sulfate de calcium allant jusqu'à 2–4% comme SO_3.
4. Dans les spécimens contenant du ciment portland au laitier de haut-fourneau on constata que la partie externe présentait des fissures importantes dues à la dilatation excessive, tandis que la partie interne restait fermement étanche, plus stable que dans le cas du ciment portland.
5. Dans la couche externe altérée, on trouva de nombreux cristaux de gypse aciculaires ainsi que de l'ettringite.
6. Afin d'améliorer la résistivité du ciment portland au laitier de haut fourneau, il a semblé désirable soit d'augmenter la quantité de gypse sans se soucier de ses modifications, soit d'augmenter la teneur en laitier jusqu'à un maximum d'environ 60%, soit de moudre le laitier plus grossièrement que le ciment normal spécialement lorsque le premier n'est contenu que dans la proportion de 30% environ.
7. Bien que la partie externe des spécimens contenant du ciment sursulfaté soit finement fissurée, la partie interne restait parfaitement intacte.

La résistivité à la neutralisation du ciment durci est importante, spécialement avec le ciment sursulfaté, parce que la neutralisation cause non seulement le risque de rouille pour l'armature en acier, mais aussi la réduction de la résistance à la flexion et de la dureté de surface.

Ces faits semblaient liés à la décomposition de l'ettringite par le gaz carbonique de l'air, avec libération de gypse. Un fin revêtement de verre soluble à la surface pouvait empêcher la neutralisation.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Tokyo Institute of Technology, Japan.

Zusammenfassung

Der Widerstand des Zements gegen chemische Angriffe ist für Japan ganz besonders wichtig, da dieses Land eine lange Küstenlinie hat, and da daher die Betonkonstruktionen häufig mit Seewasser in Berührung kommen. Der chemische Angriff durch eine 2% $MgSO_4$-Lösung wurde für verschiedene Zementmörteltypen untersucht, bei denen das Zement/Sand Mischungsverhältnis 1:4 betrug, und die folgenden Ergebnisse wurden erzielt:

1. Die Tonerdezemente, die sulfatbeständige Portlandzemente und die Portlandzemente mit niedriger Hydratationswärme sind beständig genug.
2. Die Beständigkeiten der Portlandhochofenzemente und der Portlandquarzzemente sind nicht immer so gross wie die der Normalportlandzemente und der Frühfestigportlandzemente; daher soll man in der Fabrikation der beiden erstgenannten sorgfältiger vorgehen.
3. Man kann vielleicht die Beständigkeit der Portland-, der Portlandhochofen- und der Portlandquarzzemente durch eine Zugabe von Kalziumsulfate, so dass das fertige Material bis zu 2–4% SO_3 enthält, erhöhen.
4. In den Probenkörpern, die Portlandhochofenzemente enthielten, war der Aussenteil mit Rissen durchgezogen da die Ausdehnung zu stark war, während der innere Teil, der immer zusammengedrückt war, stabiler als Portlandzement war.
5. In der veränderten äusseren Schicht wurden viele nadelförmige Gipskristalle mit Ettringit zusammen gefunden.
6. Für die Verbesserung des Widerstandes des Portlandhochofenzementes ist es wünschenswert, den Gehalt des Gipses zu erhöhen, und es ist von untergeordneter Bedeutung, welche Modifikation hier angewandt wird; man kann auch den Schlackengehalt bis ungefähr 60% erhöhen, oder die Schlacke nicht so fein wie beim Standardzement vermahlen, wenn nicht mehr als 30% Schlacke anwesend ist.
7. Der äussere Teil der sulfatenthaltenden Schlackenzemente war mit feinen Rissen durchgezogen, jedoch ist der Innenteil völlig unversehrt geblieben.

Die Widerstandsfähigkeit des ausgehärteten Zements gegen Neutralisieren ist auch wichtig, besonders beim sulfathaltigen Schlackenzement, weil eine solche Neutralisierung die Gefahr des Rostens der Stahleinlage, und auch eine Verkleinerung der Biegungsfestigkeit und der Oberflächenhärte mit sich bringt.

Das scheint damit zusammenzuhängen, dass der Ettringit schon in Berührung mit Kohlensäure der Luft unter Gipsbildung zersetzt wird. Eine solche Neutralisierung kann doch durch eine Bedeckung der Oberfläche mit einer dünnen Wasserglasschichte verhindert werden.

Introduction

There are many causes affecting the durability of concrete, such as sulfate reaction, alkali-aggregate reaction, neutralization, shrinkage or cracking due to drying, repetition of drying and wetting, frost action, and so on. Among them, chemical resistance to sea water and to neutralization by air, and the cracking due to physical causes seem to be most important, especially in Japan, because of its very long coast line and many islands which demand a vast amount of structures such as embankments and submarine tunnels in contact with sea water, and as there is a necessity to prevent the rusting of reinforcing steel in concrete in order to deal with the risk of earthquake.

On the other hand, alkali-aggregate reaction gives rise to a great problem in the United States of America, but it is not regarded so seriously in Japan, as reactive aggregate is hard to find here.

A study of the chemical resistivity was, therefore, carried out to search for a suitable cement by factorial experiments. Portland blast-furnace cement and sulfated slag cement along with portland cement were chiefly chosen for this study because slag cement is generally regarded as most resistive to chemical action and the slag available for utilization is abundant here.

Resistivity to Sulfate Solutions [1] [1]

The chemical compositions and fineness of cements and the raw materials used in this experiment are shown in table 1.

Lean mortar specimens with cement-sand ratio 1:4, using various types of cement, were immersed in 2 percent $MgSO_4$ solution, after 7 days' water curing, for a prescribed duration, then the resistivity was measured by the decrease in mechanical strength and the change of outer appearance.

The data on strength are given in table 2.

An evaluation of the resistivities of various cements is given in table 3.

The data revealed that sufficient durability was attained by alumina cement, sulfate resistant, and low-heat portland cements, while portland blast-furnace cement and portland silica cement did not always show a higher durability than normal and high-early-strength portland cement. Also, the durabilities of portland and portland blast-furnace cements might be raised by increasing the addition of gypsum up to 2–4 percent as SO_3.

Figures 1–6 show various effects on the appearance of some specimens.

The specimen with commercial portland blast-furnace cement (fig. 1) gave excessive expansion and cracks. From the factorial experiment, this

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Chemical composition and fineness of cements and raw materials tested*

Type and designation of cements	Cements tested																			Raw materials for cements prepared in laboratory				
	Commercial cements							Cements prepared in laboratory																
	Alumina cement	Silica cement	Portland blast-furnace cement	Sulfate resistant portland cement	Low-heat portland cement	High-early-strength portland cement	Normal portland cement	High sulfate portland cement	Portland blast-furnace cements								Sulfated slag cements			Granulated slag	"Beppu" white clay	Gypsum	850° C Calcined gypsum	Portland cement clinker
Cement Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19					
Chemical compositions, percent																								
Ig. loss		2.06	0.43	0.87	0.94	1.50	0.84	1.8	0.6	1.5	0.4	1.3	0.6	1.5	0.4	1.3		1.6		−1.06	8.0	20.53	0.04	0.35
Insol.		12.91	.41	.25	.25	.27	.49	.5	.3	.3	.2	.2	.3	.3	.2	.2								
SiO_2	5.55	19.23	25.01	25.40	24.01	21.59	22.51	21.3	25.9	24.0	27.8	26.6	25.9	24.0	27.8	26.6	28.0	39.2	28.0	32.10	87.7	0.22	.3	21.99
Al_2O_3	38.75	5.12	5.83	3.82	5.03	5.14	5.32	5.1	8.3	8.2	11.5	11.3	8.3	8.2	11.5	11.3	13.8	12.6	13.8	16.01	3.1	.06	.1	5.30
Fe_2O_3	16.73	2.66	2.35	4.08	4.37	2.70	3.24	3.1	2.7	2.5	2.1	1.9	2.7	2.5	2.1	1.9	1.3	1.1	1.3	1.41	.3	.02	.0	3.68
MnO			.56						.4	.4	.8	.8	.4	.4	.8	.8	1.2	1.0	1.2	1.35				
CaO	38.75	54.20	61.04	62.94	62.65	65.94	64.53	62.8	57.4	56.5	51.7	50.1	57.4	56.5	51.7	50.1	43.6	34.9	43.6	44.58	.3	32.60	40.9	65.51
MgO		1.39	2.23	.92	1.14	.96	1.01	1.0	2.3	2.3	3.6	3.6	2.3	2.3	3.6	3.6	4.7	3.8	4.7	5.44	.1	.14	.2	3.39
SO_3		1.61	1.44	.99	1.22	1.73	1.58	3.8	1.1	3.3	.6	2.9	1.1	3.3	.6	2.9	5.8	4.6	5.8		.1	46.63	58.5	.14
S			.53						.3	.3	.6	.6	.3	.3	.6	.6	.9	.7	.9	1.03				
Na_2O			.86			.24	.21	.2	.3	.3	.3	.3	.3	.3	.3	.3	.4	.3	.4	.44				.30
K_2O			.38			.30	.43	.4	.4	.4	.4	.4	.4	.4	.4	.4	.3	.2	.3	.34				.56
Total	99.87	99.70	101.07	99.27	99.61	100.37	100.16	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	101.64	99.6	100.20	100.0	101.20
Blaine fineness, cm^2/g																								
	4,220	4,750	3,390	2,150	3,600	4,720	3,050	3,250	3,660	3,860	4,270	4,470	2,930	3,130	2,820	3,020	5,450	8,130	3,330	Fine 5,090 coarse 2,660	16,850	6,910	9,110	3,570
Blending ratio																								
No. 7, portland cement								95	70	65	40	35	70	65	40	35								
Slag (fine)									30	30	60	60					87.5	70.0						
Slag (coarse)													30	30	60	60			87.5					
Gypsum								5		5		5		5		5								
Portland cement clinker																	2.5	2.0	2.5					
Calc. 850 °C gypsum																	10.0	8.0	10.0					
"Beppu" white clay																		20.0						

TABLE 2. *Compressive strength of mortar specimens*

Type and designation of cements	Commercial cements							Cements prepared in laboratory											
	Alumina cement	Silica cement	Portland blast-furnace cement	Sulfate-resistant portland cement	Low-heat portland cement	High-early strength portland cement	Normal portland cement	High-sulfate portland cement	Portland blast-furnace cements								Sulfated slag cements		
Cement No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Water curing (kg/cm²):																			
3 days	147	61	45	21	29	75	55	66	58	74	49	59	46	50	27	27	140	97	44
7 days	148	88	61	27	44	101	87	88	81	91	97	80	61	82	49	53	152	155	81
28 days	157	148	117	56	90	155	133	141	138	134	163	137	128	143	107	85	176	184	126
3 months	187	197	189	115	142	170	156	145	176	185	152	162	177	174	154	162	190	218	145
6 months	219	223	214	167	167	173	175	184	190	235	183	199	204	197	211	187	194	237	146
12 months	199	201	199	181	195	183	174	203	264	238	209	216	276	203	272	210	222	161	231
Immersed in sulfate solution (kg/cm²):																			
28 days	173	163	117	78	120	158	165	154	186	194	170	174	174	166	144	91	215	197	136
3 months	205	175	127	131	160	134	120	188	211	204	174	167	162	165	176	180	183	223	154
6 months	250	42	22	180	182	87	78	173	88	135	139	216	116	182	188	174	168	214	120
12 months	196	12	0	147	153	71	53	112	3	88	138	172	47	134	124	155	133	133	165
Ratio of strength: Sulfate solution immersion/water curing, percent:																			
28 days	110	110	100	139	134	102	117	109	135	145	104	127	136	116	134	107	122	107	108
3 months	109	89	67	114	112	79	77	130	120	110	114	103	92	95	114	111	96	102	106
6 months	114	19	10	108	109	53	45	94	46	57	76	109	57	92	89	93	87	90	82
12 months	99	6	0	81	79	39	30	55	1	37	66	80	17	66	46	74	60	83	72

TABLE 3. *Comparison of the corrosion*
(Age 12 months)

Classification based on the outward aspect of specimens		
Grade	Degree of corrosion	Cement No.
A	Thoroughly perfect	8 16 4 1
B	Almost unaltered	12 7 10 14 6 5
C	Slight cracking	11 13 15 17 18 19
D	Noticeable expansion and cracking.	9 3 2

Classification based on the decrease of the mechanical strength		
Grade	Ratio of strength: sulfate soln./water curing	Cement No.
	(Percent)	
A	>90	1
B	89-60	11 12 14 16 17 18 19 5 4
C	59-30	7 8 10 15 6
D	<29	9 13 3 2

unexpected result seemed to be due to the low amount of slag and gypsum in this cement.

With portland blast-furnace cement an altered layer 3 mm in depth was formed after 6 months, with large cracks, and many needle-shaped crystals were found in these cracks. They were handpicked and determined to be gypsum. The altered gray layer was separated from sand, with an 88-μ sieve, and was identified as ettringite by X-ray analysis. The excessive expansion and cracks were also found on the specimens containing portland blast-furnace slag and immersed in 1.8 percent sulfuric acid. The reaction products were the same as in the sulfate reaction. More detailed studies on confirmation of the reaction products and the texture are now in progress.

The specimen of commercial portland silica cement (fig. 2) gave results similar to those obtained with the above cement.

Figure 3 shows a comparison of the effect of the amount of gypsum in the low slag portland blast-furnace cement. A larger amount of additional gypsum improved the resistivity remarkably.

The effect of the amount of slag in the portland blast-furnace cement was apparent in improving the resistivity with increasing amount of slag (fig. 4).

The fineness of the slag also had a significant effect; the finer the slag the less the resistivity (fig. 5).

Observations on the resistivity of portland blast-furnace cement may be summarized as follows: the external part was severely cracked, owing to excessive expansion, while the internal part was kept intact and was more stable than in the case of portland cement free from slag. Improvement of the resistivity seems possible, provided either that the addition of calcium sulfate is increased, or that the slag content is increased up to about 60 percent, or that the slag is ground more coarsely than is the case with normal cement, especially when the slag content is only about 30 percent.

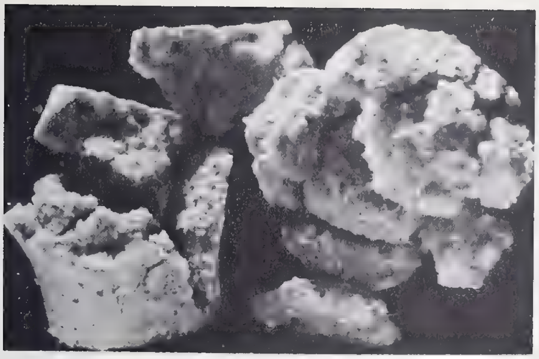

Figure 1. *Commercial portland blast-furnace cement, No. 3.*

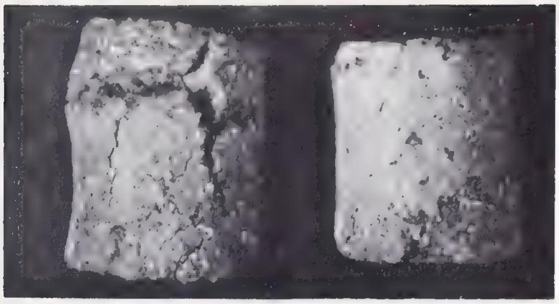

Figure 4. *Portland blast-furnace cement.*

Left—No. 9, with low slag content; right—No. 11, with high slag content.

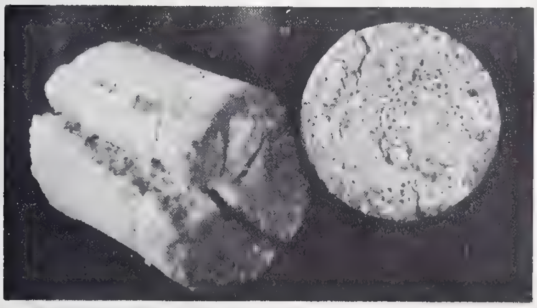

Figure 2. *Commercial portland silica cement, No. 2.*

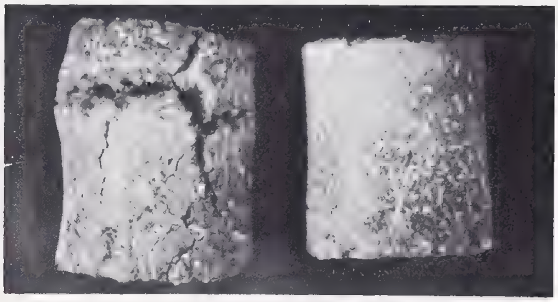

Figure 5. *Portland blast-furnace cement.*

Left—No. 9, with fine slag; right—No. 13, with coarse slag.

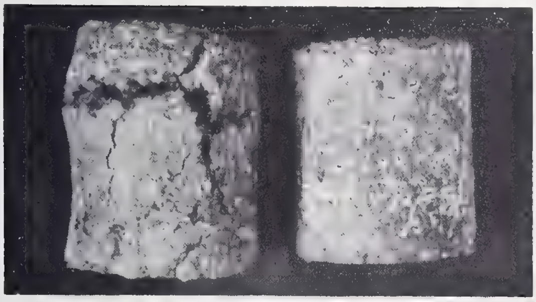

Figure 3. *Portland blast-furnace cement.*

Left—No. 9, with low gypsum content; right—No. 10, with high gypsum content.

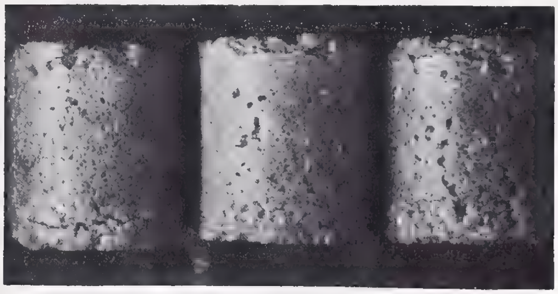

Figure 6. *Sulfated slag cement.*

Left—No. 17; middle—No. 18; right—No. 19.

(All of the specimens were 1 : 4 mortar immersed in 2% $MgSO_4$ solution for 12 months)

Thus, it becomes possible to keep the internal part of the specimen almost stable, as the result of the formation of a dense and stable protective layer over the surface. The superior durability of slag-gypsum admixture for various usages seems to be caused partly by its being coarsely ground and partly by the addition of gypsum.

Figure 6 shows a comparison of the resistivity of sulfated slag cement. Though the external part was finely cracked, the internal part remained entirely unattacked, the altered layer being not so thick as to induce heavy cracking.

Countermeasure to the Neutralization of Hardened Sulfated Slag Cement [2]

The harmful effect of neutralization is especially severe with hardened sulfated slag cement, which seems nevertheless to have suitable characteristics for the construction of massive or hydraulic structures. The decrease in bending strength and surface hardness of the hardened sulfated slag cement was ascertained to be due chiefly to neutralization, accompanied by the decomposition of ettringite, one of the main hydration products, into gypsum by the carbonic acid gas in air.

In order to prevent the neutralization, curing of specimens in gypsum solution was effective, but this method could not be practically applied to structures with vertical surfaces. Another pro-

Table 4. *Decrease in alkalinity and surface hardness of experimental cements*

Cement No.	Combination of raw materials					Depth of neutralized layer (mm)						Surface hardness (mm)					
						In air 3 months without coating			In air 3 months with water glass coating			28 days			3 months		
						Indicator											
	Portland cement	High-slag, blast-furnace cement	Separately ground slag	Calcium hydroxide	Anhydrite	Phenolphthalein	Methyl red	Methyl orange	Phenolphthalein	Methyl red	Methyl orange	In water	In air	With water glass coating, in air	In water	In air	With water glass coating, in air
	Percent	*Percent*	*Percent*	*Percent*	*Percent*												
A	100.0	--------	--------	--------	--------	0	0	0	--------	--------	--------	--------	--------	--------	--------	0.8–0.8	--------
B	97.5	--------	--------	--------	2.5	0	0	0	--------	--------	--------	--------	--------	--------	--------	0.8–0.8	--------
C	--------	100	--------	--------	--------	2.5	0	0	--------	--------	--------	--------	--------	--------	--------	1.7–1.6	--------
D	--------	95	--------	--------	5.0	1.5	0	0	--------	--------	--------	--------	--------	--------	--------	1.9–1.7	--------
E	--------	--------	79	1	20.0	4.0	.7	0	2	0.7	0	1.5–0.9	9.5–0.8	2.3–0.0	1.3–0.6	2.6–1.5	1.6–1.0

tective method was the application of a thin coating of water glass on the surfaces. A part of the experimental results is shown in table 4.

The resistivity decreased with the increase of slag content in cement. The defects of sulfated slag cement such as the rapid neutralization and low surface hardness were improved by this thin coating of water glass, to nearly the same degree as that of portland blast-furnace cement.

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Discussion

E. Spohn

I would like to comment on a remark of Mr. Kondo on the sulfate resistance of slag cements. He said: "Slag cements are generally considered as most resistive". I am not prepared to show slides on that subject, but I wish to draw your attention to a publication in Zement-Kalk-Gips, 1960, page 310: "Die Beurteilung der Sulfatbeständigkeit von Zementen nach konventionellen Schnellmethoden" by W. Lieber and K. Bleher, and, in the same issue, page 317: "Ein Schnellprüfverfahren für Zemente auf ihr Verhalten bei Sulfatangriff" by A. Koch and H. Steinegger.

For a quick sulfate resistance test, Koch uses small prisms 1 x 1 x 6 cm, made from standard DIN mortar with a water-cement ratio 0.6. After 21 days water curing, the prisms are suspended in a 10-percent solution of $Na_2SO_4 \cdot 10\ H_2O$ for 56 days. This is a sufficient time for judgment of a cement. The result is obtained after 77 days altogether. Three methods have been applied to determine the sulfate resistance:

1. Titration of the SO_3 consumption.
2. Visual observation of cracks and disintegration.
3. Flexural strength development in relation to water storage.

All three methods render similar results. The flexural strength seems to be most acceptable.

The results of these tests do not agree with the general opinion which has been quoted by Mr. Kondo. It was found that:

1. Not all slag cements are sulfate-resistant. Some behave better, some worse than average portland cements.
2. High-early-strength slag cements generally tend to inferior resistance.
3. Different slags have an utmost different effect. Therefore, the percentage of slag used does not generally indicate the sulfate resistivity.

There are on the market slag cements with about 80 percent or more high reactive slag with excellent sulfate resistivity.

A certain low reactive slag with an Al_2O_3 content as low as 11.49 percent renders an excellent sulfate resistance in a percentage of 50 to 60 with type I clinker and does even better in combination with a type V clinker. Like ordinary slag cements, this cement compares favorably with portland cements including type V, when slightly acid aggression occurs. The high resistivity is attributed to the chemical composition.

I have the impression that the miniature prism method of Koch and Steinegger should be developed to a generally acceptable rapid method for determining sulfate resistance. It could be used for all kinds of cement. The tentative ASTM test can be applied to portland cements only, but not to slag cements and others. It is known that mixing of portland cement and supersulfate cement is not permissible, and this is exactly what is done in the ASTM test, when slag cement and gypsum are mixed. The miniature prism method does not have this disadvantage. Its results so far seem closely related to the relative behavior of different cements in concrete. Cements which seem to be entirely unaffected in good concrete have no or only a slight decrease in strength and show no cracks or disintegration after 56 days exposure with the miniature test.

Discussion

H.-G. Smolczyk

We congratulate Mr. Kondo on his very interesting research work. We are in full agreement with his opinion that a higher slag content and a better composition of the blast-furnace slag cements result in improving the resistance to aggressive fluids. In addition to this we would like to mention the following:

For many years attempts have been made to estimate the chemical resistance of cements and concretes by laboratory methods. But so far these efforts have not led to satisfactory results. Thus, a universal short-time test to determine the resistance of cements and cement concretes to chemical attack does not exist. So the Anstett test, which neither in France—where this test-method came from—nor in the United States is accepted as a standard method, cannot give accurate information data of the resistance to sulfate attack or even to other chemical aggressive agents, as pointed out by Fouilloux [1].[1] Even the results of investigations carried out by groups in Germany in the course of the last few years do not supply any standard test.

Consequently it seems to be possible to determine the chemical resistance of a cement only on the basis of long-time tests or even better by experiences and observations made on concrete structures which have been in direct contact with very aggressive waters for a long time. Here attention should be paid to the large-scale concrete structures along the coast of France and Belgium, which have been very resistant to the strong chemical attack of sea water and which were built by using preferably blast-furnace cements.

There is no need of discussing the fact that blast-furnace slag cement itself is much more resistant to aggressive solutions than can be expected of the clinker minerals and their hydration products.

If one tries to avoid the more vulnerable mineral component of the portland cement—the C_3A—by increasing the iron modulus, a certain improvement of the chemical resistance of these cements to sulfate attack can be obtained. This fact is confirmed by experimental results already obtained with ore cements in former times.

On the other hand, these portland cements develop a great amount of $Ca(OH)_2$ and it is a very well-known fact that therefore they are susceptible to the effects of other chemical aggressive agents—e.g., free carbonic acid.

In the case of blast-furnace cement—especially of the low-clinker blast-furnace cement—the C_3A content is reduced by the minor clinker content. Furthermore the very low CaO content is an advantage, but a more important one is the binding of the greater part of the $Ca(OH)_2$ by the slag component, thus making these cements more resistant to the influence of any chemical attack than any portland cement with its high $Ca(OH)_2$ content could be.

By taking these facts into consideration it is evident that a blast-furnace cement must possess very good chemical resistivity. In addition to the good properties resulting from the composition of the cement, the stability of a structure in concrete-aggressive surroundings also depends on the structural advantages to be obtained by this cement. Sea-water constructions are mainly structures with large diameters. In this case the stability does not depend on the resistivity of the cement only but to a high degree on a close-grained concrete structure, especially on a dense surface of the concrete that is free of cracks.

The very low heat of hydration of the blast-furnace cement allows the construction of mass-concrete structures of great diameters without the danger of obtaining cracks by temperature (heat of hydration) stresses; and without the necessity of preparing any cooling facility.

Large-scale measurements of the temperature in concrete constructions of different diameters [2, 3, 4, 5], carried out by the Research Institute for Blast Furnace Slags at Rheinhausen, Germany, have demonstrated the great importance of a low heat of hydration of the cements, in order to obtain a concrete shell free of cracks.

Furthermore, in the case of all concrete structures for which cracks on the surface are more than esthetic defects, the rise of temperature caused by the heat of hydration is to be taken into account when deciding on concrete technological considerations and provisions.

But, after all, the favorable elastic behavior of the blast-furnace cements, as has already been learned from the increased ratio of bending-tensile strength to compressive strength, guarantees a maximum of insensitivity to cracking due to contraction or temperature stressing.

There is no doubt that the very good experience with blast-furnace cements used for structures exposed to sea-water, is based on the low heat of hydration as well as on the good elastic properties.

The Netherlands, Belgium, and France, especially, are discontinuing the production of "sulfate-resistant portland cement with a reduced C_3A-content", for in these countries there is no need of it because of the extremely good results obtained by using blast-furnace slag cement.

References

[1] Pierre Fouilloux, Über die Widerstandsfähigkeit von Zementen bei verschiedenen Angriffsarten und über die Bedeutung, die der Anstettprobe hinsichtlich des Verhaltens der Bauwerke beim Abbinden gegenüber

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[1] Figures in brackets indicate the literature references at the end of this paper.

aggressiven Wässern und Böden zukommt, Travaux, Mar. 1957, 269

[2] O. Eisemann, Zur Vermeidung von Temperaturrissen im Massenbeton, Die Bauwirtschaft, 23/24, June 1960

[3] R. Vinkeloe, Die Hydratationswärme und ihre Auswirkungen in Massenbetonbauwerken, Delivered at meetings and in the Research Institute for Blast Furnace Slags at Rheinhausen. (Publ. in prep.)

[4] Engler and Vinkeloe, Betontechnologische Vorteile einer niedrigen Abbindewärme des Zementes (Principal considerations, based on practical results in different structures). (Publ. in prep.)

[5] Hampe, Temperaturschäden im Beton, Die Bautechnik Aug. 1941.

Closure

Renichi Kondo

Mr. Spohn referred to the very recent publications on the miniature-prism method for the evaluation of cement regarding sulfate resistivity. I am glad to learn that this method gives good information in a very short period appropriate for concrete practice. It was also mentioned that the high-early-strength slag cements generally tend to inferior resistance. This result may be supposed to be due to the low slag content and finer grinding of slag in this type of cement. I cannot discuss, however, the effect of the difference in slags, as I have not done research on that point yet.

Mr. Smolczyk pointed out the valuable experience that concrete structures in Europe made of portland blast-furnace cements generally have very good resistivity against sea water. He also discussed the reasons. I have mentioned in my paper the excessive expansion of mortar caused by the reaction between hardened portland blast-furnace cement and sulfate solution. The factors governing this phenomenon were at the same time described there. I never intended to assert the general inferiority in resistance of the portland blast-furnace cements. I rather expected this experimental evidence to be useful in developing sulfate-resistant cements of much higher reliability than the ones now in production. Further fundamental investigations on this abnormal phenomenon would be also desirable.

Paper VI–S5. Durability of Concrete and Reinforced Concrete and Its Connections With the Composition of Cement, Concrete, and Construction Methods*

S. V. Shestopyorov

Synopsis (By editor)

The durability of concrete is best investigated by direct study of the frost resistance of materials and products not only in the laboratory but under the natural climatic conditions. Not only the concrete materials and the design of the concrete, but the construction methods and the curing of the concrete are important. Concrete made with freshly wet-ground clinker has certain advantages. The contraction that results from the reaction of cement and water produces minute air voids which improve frost resistance in the same way as intentional air-entrainment. Some plasticizers give beneficial results. Steam curing gives variable results and often lowers frost resistance. Many factors influence the durability of concrete and have to be taken into account. These various matters are discussed, and frost-resistance tests are reported for various concretes and for reinforced and prestressed concrete members.

Résumé

La meilleure méthode de recherches sur la durabilité du béton est l'étude directe de la résistance au gel des matériaux et des produits non seulement dans la laboratoire mais aussi sous les conditions climatiques naturelles. Ce ne sont pas seulement les matériaux du béton et sa composition qui sont importants, mais encore les méthodes de construction et la conservation du béton. Le béton produit de clinker fraîchement broyé à l'eau présente certains avantages. La contraction qui résulte de la réaction du ciment et de l'eau produit de vides minuscules remplis d'air qui améliorent la résistance au gel, ainsi que lorsque l'air est introduit volontairement. Certains plastifiants donnent des résultats favorables. La conservation à la vapeur donne des résultats variables et diminue souvent la résistance au gel. De nombreux facteurs influencent la durabilité du béton et il faut en tenir compte. Ces différentes questions sont discutées, et rapport est fait d'expériences sur la résistance au gel pour differents bétons et pour des éléments de construction en béton armé et précontraint.

Zusammenfassung

Die Beständigkeit des Betons wird vorzugsweise durch ein direktes Studium des Gefrierbenehmens der Materialien und Produkte nicht nur im Laboratorium, sondern auch unter natürlichen klimatischen Verhältnissen untersucht. Nicht nur die Betonmaterialien und die Mischungsverhältnisse des Betons, sondern auch die Konstruktions- und Erhärtungsmethoden des Betons haben ihre Bedeutung. Beton, der mit frischem nassvermahlenem Klinker hergestellt wurde, zeigt gewisse Vorteile. Die Kontraktion, die durch die Reaktion zwischen Zement und Wasser hervorgerufen wird, bringt kleine Luftporen hervor, die den Widerstand gegen Frostangriff erhöhen; dieser Effekt kann auch durch ein willkürliches Einverleiben der Luft erzielt werden. Einige plastifizierende Stoffe haben zu guten Resultaten geführt. Die Dampferhärtung kann verschiedenartige Erfolge zeigen; häufig wird der Gefrierwiderstand erniedrigt. Viele andere Faktoren beeinflussen die Betonbeständigkeit und müssen daher berücksichtigt werden. Diese Faktoren werden erörtert, und die Ergebnisse von Gefrierversuchen für mehrere Betone, Eisenbetone und Spannbetone sind beschrieben.

Introduction

Taking into account their life in the structures, reinforced-concrete constructions and details are designed and manufactured so that they may last for an indefinite time without repairs. The necessity of replacing properly designed and manufactured structures and details is caused only by their normal aging, not by destruction. This is verified by experiments *in situ*. Among the various methods of investigation of durability of concrete and reinforced concrete, including prestressed, the author considers that the best way of obtaining practical conclusions is direct study of frost resistance of materials in samples and products, including the possibility of performing experimental work under natural climatic conditions.

When investigating the frost resistance of concrete and reinforced concrete, it is impossible to limit the investigations to the materials used for concrete production and to concrete compositions. It is necessary to connect investigations of concrete durability with construction methods, including the curing of the concrete, which are often forgotten.

The highly efficient industrial methods of production of plain concrete and reinforced concrete require a more progressive technology of production of concrete mixes.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Academy of Construction and Architecture, Moscow, U.S.S.R.

Such technology includes the use of rapid-hardening, and in many cases. high-strength cements.

Change to industrial methods of production is needed both for reinforced concrete members and details and for plain concrete.

Waterproofing of concrete is a very active measure insuring primarily the creation of conditions for completion of the processes of hydrolysis and hydration of cement.

Freezing and thawing of concrete even several hundred times is insufficient for determining its durability. Concrete, during further testing, may lose its strength and be destroyed. During the combined action of water and frost, destruction which cannot be detected by a certain number of freezing-thawing cycles but which depends on the structure of the cement paste and the concrete texture may at some moment rise catastrophically. It is as if a preparatory period passes during which processes occur that determine the future destruction of the concrete. Destruction may be of various kinds; for instance, it may proceed in outside layers or inside the specimen.

Studies carried out by Powers (U.S.A.) are very interesting in relation to the frost resistance of concrete. For example, the idea is propounded of concrete destruction as a result of the hydraulic pressure developed in the concrete when the water freezes. Powers introduces many factors of great importance when considering this problem (contraction spaces, degree of saturation with water, conditions of water freezing in concrete, and others), this certainly being correct methodically. Powers, in some of his papers on concrete (cement), divides the observed destruction of this material into two kinds: internal and external (scaling). This division has also been noted in our investigations, but we consider that there are many more types of concrete destruction. The considerations on loss of concrete strength during freezing are interesting in the works of other scientists. Thus, for example, Wisey (1944) considered that loss of weight (connected with scaling or breaking of part of the sample at the edge), does not show loss of strength. We consider this point of view relative to the form of destruction correct, the latter being connected with the quality of the concrete. However, this does not mean that we agree with the opinions of Bergstrem that when the concrete is considered weak, invisible destruction of the structure is possible (loss of structural strength) in the entire sample and, consequently, in the entire volume of the structure, even though the latter is approximately the same size as the tested samples. Much work is being devoted to the problems of frost resistance of concrete (methodical work, tests with concrete, etc.). However, in our opinion, the trend and complexity which we are trying to realize, even though partially, in our investigations extending over many years, have in general been lacking. Possibilities for such investigations are widely offered to scientific workers in the USSR, where science is of unprecedented scope.

New efforts of investigators should be welcomed on this problem, which is of such great importance for construction. It should be noted that in the provisional American Standards on testing the frost resistance of concrete (C290–52T, C291–52T, C292–52T, C310–53T for different cases) the time of sample freezing varies ("slow freezing" and "rapid freezing"), as well as the conditions of freezing. Prismatic samples of concrete are tested. Principally, such an approach to testing creates the possibility of all-around evaluation of the results and, consequently, to a higher degree, approaches the needs of construction. Attention should be paid to the total duration of testing. For "rapid freezing" the highest requirement of frost resistance of concrete is 300 cycles, while, for "slow freezing," 200 cycles in water or 100 cycles in a saline solution are required. In this case it is considered that the test results may be estimated from the value of the dynamic modulus of elasticity of the frozen prismatic samples. The value of the modulus of elasticity should be not less than 60 percent of the initial value. We cannot agree with such a method of estimation of the frost resistance of concrete, and our viewpoint is verified by the results of our investigations described in the present report. Objections arise in relation to the routine use of one minimum freezing temperature during laboratory tests which differ significantly from requirements introduced in Dresden in 1886. It should be borne in mind that during recent years the use of reinforced concrete has grown immensely. Consequently, the types of structures have changed, as well as the conditions of work, even if only because construction is being carried out under natural conditions less satisfactory for the life of the material; and, besides, reinforced concrete is beginning to be widely used in industrial construction where strong aggression is possible against it. It is incorrect to consider that there is only one freezing temperature. There are as many freezing temperatures as there are types of capillaries, varying in diameter. It is natural that the denser the concrete, the smaller the diameter of the capillaries in it. When designing durable concrete, the problem arises of producing concrete with capillaries such that the water in them shall not freeze at the temperatures to which the structure will be exposed. Lengthy investigations that we have made with concrete have shown that it is possible to prepare such concrete.

As an original investigation of the frost resistance of building materials in Russia the work by K. J. Ilkevitch (1915) should be mentioned. The author of this work writes ". . . . the foregoing leads to the view that testing for freezing in various climates should be performed in different ways, namely, in conformance with the temperature conditions of each given locality. The frost resistance of materials for each locality should correspond, so to say, to its own requirements."

In 1956 a book was published by the Scientific Research Institute on Cement under the guidance of Prof. B. C. Skramtaev (author, G. I. Gorchakov). It should be noted that in this work our view on the lowering of frost resistance of concrete in conformity with the content of mineral C_3A is corroborated.

If, in many cases of practical construction, small requirements are made for frost resistance of concrete—100 cycles, for example—in many other cases a frost resistance of 1,000 cycles is considered insufficient. Knowing that it is possible to prepare concrete resisting several thousand freezing-thawing cycles, and seeking to establish the main reasons for difference in frost resistance, the following problems should be solved: (a) study of the essence of the processes proceeding in concrete that resists several thousand freezing-thawing cycles, to account for the durability of such concretes, and (b) determination of the correct criterion for the conditional freezing temperature of the water enclosed in the porous-capillary material, i.e., conditions of water freezing in capillaries of different diameters. Unfortunately for this aim, the sizes of the capillaries in concrete have not as yet been determined, and furthermore, concrete is not designed according to this criterion. We consider that the sizes of the capillaries, as well as the volume of entrained air, should be the basis of the physical properties of concrete. It is only necessary to work out a similar criterion for laboratory methods of concrete testing, modeling according to conditions in the structures. This criterion would make it possible to estimate the time factor, without which it is impossible to perform accurate design for durability of materials. We consider erroneous the view of many investigators that it is not necessary to test concrete by repeated freezing and thawing. Those proposing this view refer to the good condition of many reinforced concrete structures. Such references are unfounded, as the conditions of exposure of the materials to different climatic conditions and in different structures vary. As a rule, for proving concrete durability, the good condition of structures of mass concrete is considered sufficiently established when 200 cycles of freezing and thawing are withstood during a long period. However, no single case of destruction of reinforced concrete structures should be ignored.

We consider that the life, for example, of such prestressed reinforced-concrete products as sleepers, contact line posts, sheet piles, piles, and others should be determined only by their actual wear.

The absence of established life of structures and products leads to the lowering of requirements in projects, in standards and specifications on materials, and in construction-method rules. The durability and measures for preventive repair of structures are not taken into account.

Problems of increasing concrete durability in no case should be solved by increasing expenditures and prolonging construction delay.

For the correct use of a cement, builders should know its composition. The mineralogical composition, calculated on the basis of gross analysis, reflects the "ideal" limiting composition of the cement.

Actually, the structure of the cement clinker is characterized by the presence of certain sizes of crystals of the main minerals, connected by intermediate glassy substances.

When the degree of subdivision (grinding) changes, the mineralogical composition of the particle surface also changes. As all processes of hydrolysis and hydration proceed at the interface of the solid phase—polymineral cement—with the mixing water, this mineralogical composition is of principal significance.

Fine subdivision of cement has very important technical and economic implications. Thus, for example, it has been determined that using finely ground cements obtained by wet grinding, we basically change the structure formation in the hardened cement. By employing common dry grinding (even very fine) this effect cannot be obtained. With very fine grinding and thorough mixing of the cement paste and gypsum, the entire aluminate (C_3A) may be exposed and combined into hydrosulfoaluminate. Fine wet grinding makes it possible to free all the alite from the shielding shell of belite, while the latter, in turn, is hydrated to a very high degree. As a result, the structure of the hardened wet-ground cement obtained is of a quality differing from that of the hardened paste of dry-ground cement.

The production of fine cement by wet grinding essentially changes the process of cement manufacture by advancing it from the stage of clinker calcination to the stage of obtaining cement paste, thus bypassing the operation stage of obtaining ground cement clinker. Thus, the technology of cement manufacture, in this case, eliminates dry grinding, storage of cement in silos, and, in some cases, its packing, transportation in closed railway cars, and storage in closed premises. The clinker may be utilized directly after preparation, while for dry grinding, according to the existing conditions of cement manufacture, the cement should be stored for several days before grinding. For wet grinding, the grinding operation is transferred into the workshops of concrete plants. In these shops the most favorable conditions are created for avoiding dust from the mineral materials, thus improving hygienic labor conditions.

The manufacture of mortars and concrete from cement made by wet grinding significantly widens the possibility of improving quality on the basis of promoting accelerated and complete reaction of the hydrated tricalcium aluminate with the gypsum, thus forming hydrosulfoaluminate even during the period of the elastic-viscous-plastic condition of the cement gel.

In speaking about the new technology of manufacture, it is impossible to limit the consideration of the grinding process to the one aspect—the wet grinding. Investigation of the processes of direct structure formation in the cement gel shows the importance of combining fine disintegration with the peptization method of formation of a flocculent product, and correct incorporation of various electrolytes in the cement paste, in particular of gypsum, as well as hydraulic admixtures and nonhydraulic microfillers.

One of the most important advantages of the new technology should be improvement of uniformity of mortars and concretes manufactured at the plants. It should not be forgotten that the existing high safety factor is directly connected with the approved technology of cement, mortar, and concrete production. Variability in the strength of the control samples is taken as an inevitable evil during concreting.

It may be said that with the new technology the uniformity of concrete will be much better. Systematic and general production of mortars and concrete of uniform quality allows higher design values without raising the grade of the cement and, consequently, allows the design of structures of smaller section.

Contraction and Internal Vacuum in Cement Paste (Self-Desiccation)

It is obvious that contraction is closely connected with the frost resistance of hardened cement paste, mortar, and concrete. The possibility and degree of action in the cement paste of forces arising during the freezing of water in the capillaries and pores of the cement paste depend on the degree of their filling with water and air and on the action of newly hydrated formations. The air may penetrate into the structure of the cement paste as the reactions of hydrolysis and hydration of the minerals in the binding agent (setting and hardening of the cement paste) proceed, due to contraction, during which an internal vacuum is developed in the mass of new formations, thus making possible the entrainment of air in them, the air filling part of the volume of the capillaries and pores; the air serves as a microscopic damper during the plastic motion of ice in capillaries and pores.

The phenomena of contraction has been widely investigated in detail by V. V. Nekrasov.

The air layers in the structure of the cement paste are only effective in improving frost resistance when the solid phase with air inclusions is of high strength and does not change under the influence of the conditions of exposure.

According to the data of V. V. Nekrasov, higher contraction for one and the same time is usually observed for cement of higher mechanical strength with the same mineralogical composition but of different particle size after grinding. Increase of contraction corresponds well with increase of strength and frost resistance of cement when the size of the cement grains is lowered during grinding. This proposition is disputed by several scientists.

The introduction of an electrolyte—calcium chloride in certain amounts—increases contraction and is characterized by increase of the mechanical strength of the material. The introduction of mineral admixtures into the cement, for example, of ground quartz, lowers the contraction, changing the frost resistance similarly.

Frost resistance is directly connected with the extent of contraction of the cement paste of monomineral cements of alite and belite. For cement with a low content of C_3A, the contraction equals 14–15 ml per 300 g of cement after 30-day curing.

Further work performed for developing new premises on the relationship between contraction and frost resistance affords simple models of the frost resistance of concrete and mortars of the most various compositions.

V. V. Nekrasov showed that contraction was significantly lower for cement that was not fresh. Lengthy storage significantly lowers the total content of nonhydrated material, this lowering being confirmed by the increased losses on ignition. However, in this case, a thin hydrated shell is formed on the surface of the cement grain, and when it becomes solid, the possibility is lost of further hydrolysis and hydration of the main part of the grain which has as yet not reacted. The formation of such solid shells is most probable with grains of the smallest size. Thus, for part of the cement grains, contraction practically stops, but not for grains of larger diameter. For such grains contraction proceeds later on during their chemical peptization, which is carried out during later periods.

The formation of a vacuum in a body of concrete, caused by contraction, is described by P. E. Franzman, who shows that the water film disappears from the concrete surface due to suction into the contraction spaces.

The changing of concrete properties under the influence of different air-entraining admixtures should be considered in estimating the phenomena of internal vacuum in the setting and hardening of cement paste. Actually, in this case, an additional quantity of air is held in the concrete or mortar mix, the air being redistributed in the hardening cement paste during the contraction caused by hydration of the minerals, creating in the structure properly located air voids, not filled in the future with water in the hardened material, the water being delivered along the capillaries during saturation.

The changing of the structure of the cement paste during the process of hardening compacts the material, hampering hydration and, consequently, in this case does not allow proper consideration of the changing vacuum in the sample during long observation periods.

Let us consider some characteristic cases of destruction of samples of cement mortar during freezing and thawing, and let us connect them with data on the degree of sample saturation with water and air as a result of contraction under different conditions. In speaking about contraction and the internal vacuum corresponding to it, we cannot forget that the spaces formed at this time, at normal atmospheric pressure, either will be filled with air or will contain water. If air is in these "contraction volumes," the structure of the paste will have a shock-absorbing volume for the expansion of frozen water. The paste structure will be destroyed during freezing if these volumes are filled with water. This conclusion is confirmed by the results of *in situ* tests.

Cube specimens with 7.07-cm. edges were made of cement obtained by grinding clinker "K" in the laboratory with 3 percent gypsum admixture. The fineness of clinker grinding is indicated by the 10 to 11 percent residue on a screen with openings of 85μ. Normal one-size sand was used. Flow-table spreading of the mortar mix for a w/c ratio of 0.36, and shaking, was 130 mm.

Tests have shown the importance of air—"air dampers"—in the structure of the cement paste, formed by contraction during cement hydration.

Cement made of clinker "K" was used for a series of specimens which were immersed in water every hour for 24 hr after manufacture. These samples were then left in water for 28 days and then were vacuum-treated and transferred to the freezing chamber.

It should be noted that destruction of cement mortars with w/c=0.35–0.45, which, for usual hardening conditions are frost-resistant, was quick and complete. Consequently, common destruction beginning at the surface is a result of "deairing" of the structure of the cement paste in very thin surface layers. Under these conditions, the samples crumble—adhesion is lost between the sand particles in the surface layer, which were previously glued together by mineral gel.

If, during production of the cement paste, the mortar or concrete sample (with any w/c ratio, however low, which permits placing into molds), after molding, is left to harden in water, and is deaerated, it is easy to obtain frost-susceptible samples.

Actually, in this case the entire additional pore volume resulting from contraction, distributed equally in the material, becomes filled with water and forms capillaries acting during freezing. Freezing of such a sample, preliminarily saturated with water, creates the conditions for deep destruction of the material throughout the sample, as in this case the water when freezing cannot expand in the capillaries and pores. Consequently, any excessive water (excessive value of w/c) in the cement paste simulates the tests mentioned. This excessive amount is understood to be the water not combined with cement by chemical forces (hydration and crystal water) or by physical forces (absorptive-cohesive water) and may migrate.

Investigation of Frost Resistance of Plain Concrete and Reinforced-Concrete Products under Natural Conditions

Frost Resistance of Concrete

For estimating the frost resistance of concrete under severe natural climatic conditions, two climatic stations were organized at water basins with differing salinity. At station No. 1, the concrete was under the action of water with a salinity equal to the salt content of the ocean (20–30 g per liter). At station No. 2, soft water with low salt content acted on the concrete. Minimum air temperature at station No. 1 was −32 °C, at station No. 2, −45 °C; the water had a temperature from +1 °C to 4 °C. When calculating the freezing-thawing cycles the number of passes through 0 °C was taken into account. When considering passing through −15 °C and lower, for station No. 1 the number of cycles was decreased by about four times.

A large number of specimens were made of gravel consisting of frost-resistant grains and of cement with frost-resistant structure of the cement paste.

The surface of the specimens was polished, coated, penetrated with bitumen, and painted with ethanol varnish. The samples were made of different binding agents and aggregates and were tested after long hardening periods. The number of specimens tested under natural conditions at the two stations was over 10,000. The resistance of the specimens was estimated from their external appearance by rating points (table 1), and, for part of the specimens, by repeated tests of mechanical strength.

The approved methods are provisional, but they permit rapid and simultaneous testing of a large number of concrete compositions. Estimation of the condition of the specimens by the 10-point system permitted daily determinations with sufficient accuracy. The provisional criterion for beginning of destruction of the specimen was the moment corresponding to passage from the ninth point to the eighth point. As the defects of the specimen appeared, testing for ultimate strength was stopped. As the specimens were not moved from place to place during testing, it was possible to observe the destruction process of the specimens at all stages. Determination of the strength of the specimens should not be overestimated. In many cases, significant scattering of test results was observed, this being natural in view of the changing quality of the concrete surface. On the other hand, lowering of the strength of the specimen under the influence of mechanical causes leads to the appearance of external defects. Separate tests were carried out for finding the strength of the specimens after a certain number of freezing-

TABLE 1. *Scale of frost resistance by rating points*

Estimation of frost resistance in points	Concrete: type of destruction	Estimation of frost resistance in points	Mortar: type of destruction
10	No destruction.	5	No destruction.
9	Small changes: scaling of sides, beginning of edge rounding.	4	Small initial crumbling of edges and corners.
8	The same, with pits due to destruction of grains of non-frost-resistant rocks.	3	Beginning of destruction of sides.
7	The same, only to a higher degree; specimen becomes rounded.	2	Pronounced destruction of edges at corners and sides.
6	Sample loses its cubic shape; destruction of sides for 30–40 percent, appearance of cracks and breaking of corners.	1	Presence of cracks and violation of monolithic structure of sample.
5	Destruction of all corners. Destruction of sides by 60–70 percent.		
4	Destruction of sides by 80–90 percent.		
3	Sides distinguished with difficulty.		
2	No sides seen.		
1	Complete rounding of specimen.		

thawing cycles. However, this method of testing is not justified, for at the time of the test one part of the samples is being strongly destroyed, and its strength cannot be determined, while for the other part no signs of destruction have as yet appeared. When testing reinforced-concrete sleepers, drawings were made of their external appearance, thus facilitating the analysis of causes of destruction when comparing the condition of the concrete cubes and estimating the operation of the technologic equipment, primarily the vibrating platform, and the approved technologic process.

When the concrete in various structures experiences severe climatic conditions, it may pass during one year through several hundred freezing-thawing cycles. At station No. 1, during one day, it is moistened with water twice and at station No. 2 six or seven times. Therefore, for these cases it is important to estimate the resistance of the concrete by the number of freezing-thawing cycles rather than by its resistance during many years of exposure.

Testing of cubic samples, for instance, with edges of 20 cm, in this case completely simulates the working conditions of concrete in non-mass structures, for example in sleepers, communication line posts, posts of electric power lines and contact line posts, sheet piles, piles and beams of such structures as moorings and piers, airfield and road pavements, curbstones, slabs on revetments, etc.

The destruction of concrete cubes of plastic mixtures, as a rule, begins from the upper edge (smoothed edge of specimen) where, due to slight sedimentation of the concrete mix, there is more water than in the rest of the specimen.

Destruction of non-frost-resistant gravel grains in the concrete is noted not only at direct contact of the concrete with water (with permanent capillary suction), but also during periodic action of atmospheric precipitation on the concrete. In tests over a period of 20 yr to determine the weather resistance of concrete of different compositions, performed with 1.5-m and 2.0-m cubes, several interesting features were observed relative to the destruction of non-frost-resistant gravel grains. Thus, for concrete cubes of portland cement with cement contents of 400 kg/m^3 and 280 kg/m^3 and alumina cement with a cement content of 280 kg/m^3, after about 7 yr signs of destruction of the concrete surface began to appear at locations of weak gravel grains, while for samples made of sand-pozzolan cement no destruction was observed.

Even when the concrete was gradually or incidentally saturated with atmospheric moisture and the specimen did not absorb liquid water, the presence in the structure of the cement paste of active capillaries caused destruction of the concrete texture due to freezing of the weak rock material in it, in the same way as when the concrete was constantly moistened with water, but in the latter case destruction proceeded at a higher rate. If "passive" capillaries prevail in the structure of the cement paste, through which the water flows freely, non-frost-resistant cement paste exposed to the same conditions should not be destroyed.

For concrete existing under conditions such that the aggregate may be saturated gradually with water, and the concrete experiences systematic freezing and thawing, non-frost-resistant rock materials should not be employed. The influence of contact density may be clearly seen according to the results of tests of concrete with large-size sandstone aggregate. The concrete has a lower frost resistance, even though the frost resistance of the rock is high. Checking of contact density was performed by determination of the impermeability of the concrete.

After 3,000 test cycles, the concrete samples saturated with bitumen were well preserved (9–10 points) (samples of low-aluminate portland cement of one cement plant with crushed gabbro and dolomite, $w/c=0.65$ and 0.68). This result demonstrates the high resistance of concrete in which the capillaries filled with bitumen are hydrophobized after hardening of the cement paste.

After 3,600 test cycles, the specimens with $w/c=0.68$ were destroyed. (They were made with crushed tough dolomite.)

The problem of the curing of hardening concrete is closely connected with the strength of the concrete and its resistance to various aggressive physical and chemical factors of the ambient media. It would be very foolish, when considering concrete resistance, to limit the requirements regarding it to an incomplete one-sided specification of the material composition and its quality for estimating the resistance of the concrete, without paying attention to the technology, in which the concrete composition, its molding, and the care of the concrete up to a certain time in the hardening period, with other conditions invariable, are of decisive importance.

Cement is a half-finished product, and the technical properties of the cement paste in the mortar or concrete are developed by the builder at the construction site. The idea of absolute and not relative value of concrete strength, obtained during the testing of concrete cubes, leads to underestimation of the importance of insuring the required thermal-moisture conditions for hardening of the cement paste in the mortar or concrete. There are examples where concrete of higher mechanical strength has lower frost resistance than concrete with relatively lower strength. It is important to know the relative strength—the ratio of the actual strength to the strength which would be obtained with the given cement under optimal conditions of manufacture, formation, and curing.

It is possible to show an example of destruction after 15 to 20 test cycles of several concrete specimens with an ultimate strength of about 400 kg/cm² made of alumina cement. Such insignificant frost resistance of concrete is explained by the fact that this concrete was placed under water.

There are several cases of defective concrete in various engineering structures after a relatively short period of operation. Destruction began owing to the use of concrete which conformed only with the requirements on strength.

Concrete begins to freeze in zones of the structures which are systematically saturated with water during the winter period. Repeated freezing and thawing of concrete leads to its destruction and to the need for repairs of the structure. It should be noted that concrete which was used for these structures resisted standard freezing tests.

Due to the increased use of prestressed reinforced-concrete structures, investigations have been started on the frost resistance of stressed concrete.

For these tests, cement "B" was used (table 2). It is of the high-aluminate type ($C_3A=10.5\%$). Before making the samples the cement was stored for six months, which significantly lowered its activity. Before the specimens were made, the cement was reground with a small number of balls in a ball mill.

The mineralogical content of the cement, in percentages, was: C_3S, 50; C_2S, 20; C_3A, 10.5; other minerals, 19.5; no free lime.

Sand with a fineness modulus of 2.2 containing 2.5 percent of clay and silt was used for making the specimens. The voids in the sand amounted to 38 percent. Crushed granite was used as the coarse aggregate. The voids in the crushed rock in the loose condition amounted to 42 percent. For some concrete compositions, the influence of a plasticizer of sulfite cellulose extract was investigated, as well as the quantity of gypsum and active mineral admixture of tripolite, with respect to variation of the frost resistance of the cement paste structure. The lower limit of water content was determined by the consistency of the concrete mix on a CM–475 vibrating platform with amplitude of oscillations from 0.3 to 0.6 mm. As the cement content in the concrete increased, the minimum water content correspondingly increased. Thus, if the cement content was 50 kg/m³, a water content of 110 kg/m³ was sufficient for obtaining a concrete mix of the required consistency. When the cement content increased to 500 kg/m³, the water content was increased to 140 kg/m³. Twelve samples were made of each concrete composition (table 3).

Before the frost-resistance tests, the specimens hardened for 28 days under normal conditions, and then were in the air for 310 to 340 days.

All twelve specimens were molded simultaneously on the CM–475 vibrating platform. The molds were fastened to the vibrating platform by mechanical fastenings and electromagnets.

It was determined that by future care of the concrete it is impossible to remedy the defects in the cement paste structure which appear as a result of violation of the thermal regime required for proper progress of the processes of cement hydrolysis and hydration after mixing. As the plasticizer somewhat retards the hardening process in its initial stage, it is natural that violation of the hardening conditions of the specimen is reflected to a high degree in the structure of the plasticized concretes. Investigations have shown how the porosity of samples of a cement mortar made with

TABLE 2. *Characteristics of portland cement "B"*

Time of testing	Fineness of grinding (percentage residue on screens)		Normal consistency		Setting time		Liter weight		Ultimate compressive strength of mortar specimen (1:3) for various hardening times			
	No. 021 (900 openings per sq cm)	No. 0085 (2,900 openings per sq cm)	Cement paste	Mortar	Beginning	End	Loose	Dense	1 day	3 days	7 days	28 days
			Percent	*Percent*	*hr:min*	*hr:min*	*g/liter*	*g/liter*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
When received from factory	1.0	4.52	26.75	7.69	4:30	5:30	1,025	1,256	199	371	490	565
After aging	-------	-------	21.50	6.37	3:55	6:55	-------	-------	128	303	408	535
After repeated grinding	.1	4.52	29.0	8.25	3:35	6:15	1,025	1,256	91	249	393	496

TABLE 3. *Concrete components for portland cement "B"*

Cement	Components of concrete			w/c	Content of cement admixtures	
	Water	Sand	Crushed stone		Gypsum	Tripolite
	kg/m³	*kg/m³*	*kg/m³*		*wt %*	*wt %*
250	110	approx. 575	approx. 1, 490	0. 44	---------	---------
	120			. 48		
	130			. 52		
	140			. 56		
	150			. 60		
323	110	approx. 476	approx. 1, 490	. 34	---------	---------
	120			. 37		
	130			. 40		
	140			. 43		
	150			. 46		
400	120	approx. 452	approx. 1, 490	. 30	5 and 10	---------
	130			. 325		
	140			. 35		
	150			. 375		
	160			. 40		
	180			. 45		
450	130	approx. 486	approx. 1, 370	. 29	---------	10, 20, and 30.
	140			. 31		
	150			. 33		
	160			. 356		
	180			. 40		
500	140	approx. 300	approx. 1, 490	. 28	---------	---------
	150			. 30		
	160			. 32		
	180			. 36		
	200			. 40		

standard sand (composition 1:2, w/c=0.29–0.23) increases in case of air hardening at a relative humidity of 75 to 80 percent and in a water-saturated atmosphere. These tests were carried out on cement from "K" clinker obtained in the laboratory by dry grinding. The fineness of grinding of cement containing 5 percent of gypsum, as measured on the Tovarov apparatus, was 4,000 cm^2/g.

The features of concrete (mortar) hardening kinetics as affected by admixtures of plasticizers should also be noted. These results confirm our hypothesis of retarding of hardening processes of the cement paste when introducing plasticizers. During the beginning of hardening (5 days), even when hardening at 100 percent relative humidity, the samples containing 0.2 percent plasticizer had a higher porosity than samples without a plasticizer and with 0.1 percent plasticizer. This observation suggests that the structure of cement paste of low-aluminate clinker worsens when 0.2 plasticizer is introduced. However, after 90 days of hardening, the porosity of samples with 0.2 percent plasticizer was lower than for the others. During normal hardening conditions in water the porosity of samples is significantly lowered after some time. When the samples are airhardened without moisture saturation their porosity systematically increases (table 4). Any increase of porosity influences the durability of the concrete. Therefore, even for optimal hardening regimes, it is important what structure of cement paste is designed. Moreover, when designing concrete, increase of porosity is of some importance since it leads to significant worsening of the structure of the cement paste and the texture of the mortar due to incorrect care of the molded material.

TABLE 4. *Influence of relative humidity on porosity of cement mortar*

Relative humidity, percent	Initial w/c	Total porosity at different times of hardening			
		2 days	7 days	28 days	90 days
75–80	0. 29	12–13	13–14	14–15	13–15
	. 27	8–11	12–15	14–15	14–15
	. 25	12	16	17	16
	. 23	18	18	17	17
100	. 29	8–10	8–10	5–9	4–5
	. 27	7–9	9–10	6–11	5–6
	. 25	12	12	9	4
	. 23	16	8	9	7

In the case considered, the porosity is increased due to a change in the quantity and size of the pores, thus varying the mechanical strength of the concrete. This change is clearly seen when the strength of concrete is determined at an age of at least 28 days. However, due to the hardening features of such minerals as tricalcium aluminate or aluminoferrite, the change of strength at the beginning (1–7 days) cannot be used to judge the variation of porosity.

The preceding shows the importance of curing in concrete hardening. It should be borne in mind that concrete with a high initial w/c, hardened for a long time under normal "aging" conditions, has a lower porosity and better structure than concrete with a lower w/c, hardened under conditions of insufficient humidity. The mentioned feature is of extraordinary importance for high-strength concrete of "stiff" concrete mixes, always being taken into account.

For certain climatic conditions it is possible to produce frost-resistant concrete by designing and preparing concrete with passive capillaries.

Due to the creative cooperation of the Department of Building Materials of the All-Union Institute of Transport Construction with scientific workers of the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of Czechoslovakia (Prof. B. Gazar, B. Counovsky, A. N. Slovatsky, J. Jambor, and others), it was possible to investigate two plasticizers of the sulfite cellulose extract type, "C" and "vusal." This study is most interesting since, in spite of the various investigations widely carried out, the role of the plasticizer, universal in its action on the cement paste (mortar or concrete mix) and the hardened cement paste obtained from it (table 5), has been underestimated by some specialists in foreign countries.

These plasticizers were proposed and investigated by scientists in Czechoslovakia. Several papers have been published on the use of these plasticizers for construction. Wide investigations have been carried out in Czechoslovakia by J. Jambor.

The papers of the Czechoslovakian scientists noted the excellent properties of these plasticizers, which are similar to the properties of Soviet plasticizers. Simultaneously, some abnormal cases were noted when working with these plasticizers.

TABLE 5. *Influence of type "C" plasticizer on frost resistance of concrete*

Portland cement (laboratory index)	Amount of plasticizer (percentage of cement weight)	Number of freezing-thawing cycles	Estimation of condition of specimen	Ultimate compressive strength	
				Standard	After freezing
			Points	*kg/cm²*	*kg/cm²*
"Bl"	0.1	120	10–10p		495[a]–562
		222	10–10p	490–634	460[a]–544
		319	9–10p		412[a]
	.2	222	10		432–600
		350	10	600–639	386–622
		467	9–10		510–535
		567	9		540–568
	.3	222	10		443–547
		350	10	466–540	565–595
		467	9–10		550–600
		567	9–10		420–550
	.4	222	10		512–533
		350	10		466–497
		467	9–10	440–610	502–525
		567	9		402–500
"B"	.1	102	10		480–512
		193	9–10	435–436	428–450
	.2	193	10		445–512
		326	9–10	505–626	394[a]–520
		417	8–9		364[a]–386[a]
	.3	193	10		480–628
		326	9–10	505–610	518–575
		417	9		490–575
		106	10	476–500	396–440
		417	8		395–455

[a] Visible crack network on specimen.

Note: The best concrete composition for the last test (Mar. 1960) passed over 2,000 cycles without changing the external shape of the specimens.

The study of these cases confirms what is said above on the necessity of estimating the quality of the plasticized cements. Some cements have delayed initial and final set, especially at high w/c ratio. Delay of the hardening processes may be observed by determining heat emission.

The plasticizers positively influence impermeability, chemical resistance, and frost resistance of concrete, and lower the absorptive capacity of concrete (mortar). It is considered that the plasticizers, in particular type "C," "partially increase" the bond with the reinforcement; it is advised that this admixture be used for highly reinforced structures. The application of plasticizers improves the transportability of the concrete mix, insuring the absence of segregation and improving the quality of the injected mortar.

The introduction of plasticizers into concrete (reinforced concrete) with air-entraining (air-retaining) agents is a very effective technical measure. All kinds of cement should be manufactured with such admixtures. The application of plasticizer dosages to concrete, as mentioned above, should be performed only in accordance with the active mineralogical and chemical content of the cement.

The Frost Resistance of Reinforced Concrete Structures

Reinforced-concrete railway sleepers, parts of communication-circuit line posts, blocks for prefabricated tunnel lining, and roof slabs were delivered to station No. 2 for checking the frost resistance of reinforced-concrete structures. All products were made with sized crushed granite. Concrete of similar composition was used for manufacturing reinforced-concrete products parallel with testing of cubic specimens. Comparison of the results of testing of cubes and products affirm the following:

1. The influence of the molding conditions of concrete mixes.
2. The influence of the arrangement of reinforcement in the concrete on the frost resistance of products. In particular, during tamping of mixes special attention should be paid to the molding of the protective layer of the article, including the side surfaces of the sleepers. In this case it is necessary to maintain vibration of the mix such that the side walls of the mold do not move horizontally, causing the entrainment of large air bubbles in the mix.

It was only natural that the previously employed system of estimating the condition of structures should be changed, and this was accordingly done. Two kinds of destruction of different intensity may be observed. One, designated by the letter "a" relates to the destruction of sleepers at the sides with destruction of the protective layers along the entire length of the sleeper. Each kind of destruction is estimated according to a six-point scale, which fixes the condition of the sleeper ends (end 1 and end 2). Estimation in points is given in the form of a relationship of the points for each end of the sleeper. All cases of destruction were observed during the last five years of investigation of frost resistance when studying the problem of different methods of tamping the concrete mix. During the testing process it was required to find whether the proposal of the author of the present report was correct as to the possible difference in quality of concrete of one and the same composition, molded on one and the same vibrating platform, only with different oscillations of the mold.

Testing of sleepers for frost resistance was performed at climatic station No. 2. Significant changing of the sleeper edges was noted only after 400 cycles. At this time the ratings were estimated (at the ends of the sleeper) for two sleepers: $\frac{\mathrm{IIa}}{\mathrm{Va}}$ (sleeper No. 1) and $\frac{\mathrm{I}}{\mathrm{IIa}}$ (sleeper No. 2), while after 450 cycles the ratings were $\frac{\mathrm{IIa}}{\mathrm{VIa}}$ and $\frac{\text{unchanged}}{\mathrm{Va}}$. In this case the highest rating is I.

The condition of both ends of the sleeper molded without shifting and repeated vibration, at 400 cycles was estimated as IIIa, and at 450 cycles as IIIb.

Repeated testing of frost resistance of sleepers manufactured from a concrete mix containing 450 kg/m³ of cement with a plasticizer (concentrated sulfite cellulose extract) gave similar results. Testing of these sleepers is being continued.

Cubes of size 10×10×10 cm from a concrete mix of the same composition were molded on a laboratory vibrating platform and tested for frost resistance in the laboratory freezing chamber. After 450 cycles, hair cracks appeared on the specimens. It should be noted that one end of sleeper No. 2 shows no signs of destruction, consequently, during molding of sleepers on the vibrating platform it is possible to obtain a concrete, the frost resistance of which is higher than for the "standard" specimens manufactured on the laboratory vibrating platform.

For samples of sleepers used for testing, freezing was performed on cubes of size 10×10×10 cm made from the same concrete mix as the reinforced-concrete sleepers. The water content in the concrete mix, in the samples used for freezing, was 105–160 kg, and the cement content was 350–500 kg/m^3. All sleepers except one were tested after 117–243 days. Testing showed that destruction of the sleepers begins as a rule at the face and side surfaces. Destruction proceeds on the sections where the concrete is not uniform. The product behaves as though made of different concretes, even though this effect does not appear under static testing. As indicated, it has different mechanical strength and frost resistance or sulfate-resistance, etc. During analysis of the results of testing the first 34 sleepers of a large lot delivered for testing, heterogeneity of the concrete appears as follows. During the given period of test, opposite ends of the same sleeper undergo destruction with different intensity; as a rule, destruction begins at the faces of the sleeper and at the side surfaces along the protective layers of concrete; sleepers molded from a concrete mix on vibrating platforms have higher frost resistance than sleepers molded by other methods; sleepers molded from a concrete mix with lower water content (lower w/c ratio) on vibrating platforms have higher frost resistance than sleepers from mixes with higher water content. The destruction of the latter has a local character, if the concrete mix has a low consistency limit, with low water content (less than 150 kg/m^3 of water). For example, in two sleepers, at the 85th cycle destructions rated at IIa were noted. These destructions, up to 400 cycles, did not develop further; but as the tests proceeded, the area of these places was destroyed. Consequently, the sleeper had non-frost-resistant weak sections after 85 test cycles, even though as a whole, the sleeper was frost-resistant. One of these sleepers was removed from tests of frost resistance after 490 cycles with rating I/IIIb and passed tests of multiple repeated loading which it resisted. These tests, as well as the testing of cubes, showed that ethanol varnish cannot protect concrete with defects in the structure of the cement paste and in the concrete texture. However, for manufacture of a good quality of sleeper, it is possible to produce concrete of high frost resistance. Coating the concrete with ethanol varnish cannot compensate for deficiencies in the quality of the materials used, the concrete mix, and the concrete. Coating partially prevents defects caused by unsatisfactory care of the hardening concrete. For example, coating the concrete with ethanol varnish eliminates the formation of shrinkage cracks, and for other conditions it aids in production of concrete of higher frost resistance.

Testing sleepers with stressed coil reinforcement, made by standard technology, with tamping by suspended vibrators, does not show good results. Sleepers of concrete containing 350 kg/m^3 of cement, with 2 percent of $CaCl_2$, and 126 kg/m^3 of water were covered with cracks at the 42d cycle. The concrete was severely destroyed under weak impacts, this being connected with nonobservance of the rules for curing of the concrete. Testing of frost resistance of sleepers with stressed wire reinforcement was performed by the standard technology production methods. Molding of the sleepers was carried out by internal electromechanical vibrators with motors on one shaft, CNJIS-type, and additionally by surface vibrators.

Testing of about 120 reinforced concrete sleepers at the climatic station showed that only "stiff," properly molded concrete mixes insured preservation of the sleepers under these conditions. Thus, for example, the concrete of sleepers with 150 kg water and 350 kg/m^3 cement, had the lowest frost resistance according to the results of testing of cubes which were destroyed after approximately the same number of cycles as the sleeper. If, for mass structures with great thickness of the protective layer, the concrete is destroyed by cracks or crumbling, scaling of the surface does not have a catastrophic character; but such destruction of concrete is not allowable in precast reinforced concrete structures, especially with prestressed wire reinforcement where the thickness of the protective layer is 15–25 mm. It should be noted that destruction of the concrete in the sleeper depends closely on the strength of the concrete after one day. The lower the strength, independent of the concrete grade, the lower the frost resistance. This behavior is only natural, until we can create hardening conditions for the sleepers of the same kind as for the control cubes and consequently obtain the same structure in relation to frost resistance during a long hardening period as for sleepers with high one-day strength. This problem is very important for practical purposes. Testing at the climatic station of the frost resistance of the control cubes for several sleepers is also interesting in some respects. In the following table are given the results of these tests, which were performed at the same time as the testing of the sleepers.

Two tenths of one percent of a sulfite-cellulose-extract plasticizer was introduced into the concrete.

As can be seen, on the basis of results up to the 128th cycle none of the cubes showed signs of lack of frost resistance of the outer layers of concrete, while local destruction was noted on one of the sleepers at the end (rating IIa). At the 176th

Results of tests on frost resistance of control cubes and of several sleepers

Item No.	Content of water and cement	Estimation in rating points, of condition of samples during the indicated number of test cycles							
		80	128	176	240	340	352	408	464
	kg/m³								
1	127:350	10	10	9	8	7	6	5	3
2	130:350	10	10	10	9	8	8	7	5
3	135:450	10	10	10–9	9–8	7	6	5	3
4	140:400	10	10	10	10	10–8	9–7	9–7	8–6

cycle, parts of the cubes were partly destroyed (rating 9), while the condition of the ends of both sleepers was estimated at IIIa. At the 400th cycle, destruction of the cubes reached rating 5 and, of the sleepers, rating IVa. At this point, the destroyed depth at the faces exceeded 11 cm, the reinforcement was bared, and large cracks appeared as well as a network on the part of the sleeper under the rail. At the 464th cycle, destruction was significantly enhanced, as was indicated for the cubes by a rating of 5 and for the sleepers by a rating of Va. The frost resistance of concrete cubes and sleepers hardened under the same unfavorable conditions was lower than that of concrete of the same composition hardening under favorable conditions. The tests have shown that it is possible to attain complete agreement of test results for cubes and products of the same concrete mix if there is elimination of defects connected with lack of uniformity of mix tamping during molding of reinforced concrete products and the arrangement of the reinforcement in the concrete.

Testing of sleepers of concrete with a high content of cement (550 kg/m³) and water (165 kg/m³) shows that with poor curing of the hardening sleepers the concrete does not possess high frost resistance. At the 100th cycle, sleepers of such concrete of rapid-hardening cement show clear signs of destruction—scaling of edges and corners below the rail. Calcium silicate sleepers, at the 100th cycle, also show insufficiently high frost resistance. At this time, splits form at the corners and edges and adjoining parts of the faces. Destruction of calcium silicate sleepers is similar to destruction of samples of mortar with partial de-aeration during hardening in water. This is only natural, as the effect of contraction for portland cement and calcium silicate differs, leading to different destruction procedures for these materials and different durabilities. It should be noted that coating, with ethanol varnish, a sleeper made of concrete containing 140 kg/m³ of water and 450 kg/m³ of cement with 0.2 percent plasticizer, results, after 600 cycles, in a good external appearance. This sleeper did not have any embedded members of wood (drift sleeves) which should in no case be allowed in reinforced concrete structures. The face parts of the sleepers should not have weakened places due to shifting of wires and anchor sections during manufacturing. During the testing of double-bar sleepers it was observed that destruction of concrete started at the places of fastening of the bar ends. Bunches of wires cause severe destruction of the sleepers.

On the basis of the preceding presentation it is considered that the problem of manufacture of prestressed reinforced concrete sleepers having a durability of 100 years and more, and capable of resisting over 400 freezing-thawing cycles, is solved.

Let us now consider some of the results of initial tests with other types of structures. The test samples of structures were posts made in wooden molds inserted into special steel shells. Molding was performed on two nonsynchronized five-ton platforms, type CM–476. The steel shells were fastened to the vibrating platforms by means of wedges. In this case the concrete mix was tamped without additional loadings. At the beginning of testing the concrete had different hardening periods, from 1 to 2 years. The tension of reinforcement was performed on the mold during concreting of the posts in a horizontal position. Besides these posts, the same type of prestressed post was tested without steaming and manufactured by standard technology. Wire tensioning was performed on special stops. The posts were made in steel forms on a vibrating platform, only this time in a vertical position. The thickness of the post walls was 50 mm.

On the basis of test results at the 100th cycle, only one specimen was destroyed. At the 200th test cycle, two samples, Nos. 1 and 3, did not show any signs of destruction of the concrete surface. On the other concrete specimens, only insignificant signs of destruction were visible in the monolithic structure in the form of disorientated weak cracks and longitudinal cracks. At the 300th test cycle, the strongest samples (Nos. 1 and 3) showed the same defects. Further destruction appeared in the form of crumbling of the concrete at the edges and faces. For samples Nos. 1 and 3, this crumbling was observed at the 400th cycle, and for the rest, at the 350th cycle. At 800 cycles all structural members were entirely destroyed, baring the reinforcement.

Testing of frost resistance was also performed with test samples of prestressed corner members for telegraph posts. The corner members (reinforced concrete parts in the form of wide flange angles) were made with "rapid" cement without gypsum. This cement had been stored for 1.5 years, but the time of initial set had not changed. For correction of this deficiency, gypsum (3 percent) was added. Concrete for corner members contained 158 kg of water and 400 kg of cement per cubic meter. During the first 14 days, the corner members hardened under conditions of usual production care, and then under natural conditions. At the age of 28 days, the corner members were tested for frost resistance. The strength of control samples R_{28} under compression was 460 kg/cm². At the 100th cycle of testing, severe destruction of the corner members began.

When steaming concrete or during common hardening in open air, worsening of hardening conditions is possible, leading to lowering of the content of lime in the concrete with simultaneous lowering of concrete density. Therefore, that type of hardening is considered the best which ensures observation of the mentioned conditions. We consider that in this case the best cement should be made by fine wet grinding, creating the conditions for more effective progress of processes, insuring dense, corrosion-proof structures.

After the 100th freezing-thawing cycle, definite advantages were evident relative to the concrete in post No. 3. Thus, when the concrete of posts Nos. 1 and 2, at a rating of several points, was crumbling, and the reinforcement was bared, the concrete of post No. 3 did not have such destruction. Cracks and networks of hair cracks were observed on all posts.

Special attention should be paid to the problem of preservation, near the reinforcement, of an alkaline medium. However, for some depth of the protective layer of concrete, especially during low-quality molding with "stiff" steaming regime, the lime is rapidly combined with carbon dioxide, this not being allowed for in establishing the entire depth of the layer.

When making sleepers and posts, special attention should be paid to correct selection of the time of transmission of stresses to the concrete, and for preventing water seepage paths. The face parts of the sleepers, posts and other structures should be tamped thoroughly. It is important to select the amplitude of oscillations of the vibrating platform, confining it to the range of 0.3 to 0.6 mm (for 3,000 oscillations per minute).

The amplitude of oscillations of the vibrating platform (vibrating stand) should be selected in a practical way, on the basis of the working conditions for molding. The amplitude of oscillations, in particular, depends not only on the weight of the form, and the mix, but also on the thickness of the tamped layer. Resonant oscillations, which create impacts and, consequently, prevent bond of the reinforcement with the concrete, should not be allowed. The optimal value for obtaining dense concrete, in application to concrete mixes with low consistency limits, should be considered (for example, 110–120 kg of water, 350 of cement per cubic meter). Molding of such concrete mixes should be performed on a double-frequency stand, choosing the optimum amplitude of oscillations and employing a dynamic additional load. Before tamping and during the first stage of tamping, the concrete mix should be in a vacuum. When tamping mortar and concrete mixes (with aggregate of various sizes), the thickness of the layer of the mix is of decisive importance.

In this respect, the tamping of concrete mixes is somewhat difficult in forms of variable section—in steel forms of I-beam section, in particular. A lower amplitude of oscillations is needed for the lower flange, while a higher amplitude is needed for the web. The flange has a variable height and it is, therefore, advisable that the amplitude of oscillations of the mix should vary with the height. It is, therefore, important to adjust the tamping conditions by using different frequencies and their combinations, since changing the oscillation amplitude at one frequency is still impossible.

Contact line posts with stressed deformed reinforcing bars, manufactured in the centrifugal machine at the laboratory shop of our Institute, were sent to climatic station No. 2 for testing for frost resistance. The posts were tested in half-immersed horizontal condition. Testing is now in the stage (300 cycles) where destruction of the inner layer of the post wall may be seen.

The duration of centrifuging was 20 min. Steaming of molded posts was performed at 80 °C. The surface of post No. 3, some days after steaming, was coated with two layers of perchlorvinyl enamel XB–26 (table 6).

Table 6. *Characteristics of cement "B" and concrete of experimental centrifugal contact line posts*

Post No.	Cement characteristics			Concrete components after centrifuging				Sulfite cellulose extract	Steaming regime
	Activity	Normal consistency	Term of storage	Cement	Water	Sand	Crushed stone		
	kg/cm^2	*percent*	*mo.*	*kg/m^3*	*kg/m^3*	*kg/m^3*	*kg/m^3*	*percent*	*hr*
1	600	28	45	399	172	477	1,370	0.2	During 4 hrs 3+8+0
2	620	29.5	0	400	179	520	1,320	.2	During 8 hrs 3+10+0
3	595	29	25	414	149	585	1,310	.2	During 60 hrs 3+8+0
4	600	28	15	412	157	530	1,340	.2	During 4 hrs 3+10+0
5	600	28	15	404	175	510	1,300	.2	During 4 hrs 3+9+7

Notes:

1. Support No. 3 is coated with a steam-insulation layer.
2. The strength of each post after 28 days, in kg/cm^2:

	No. 1	No. 2	No. 3	No. 4	No. 5
Initial	368	320	410	366	465
After centrifuging	445	539	440	430	---------

3. Posts Nos. 1 and 2 are reinforced with prestressed wires; the others are reinforced with bars, prestressed before concreting.
4. At one and the same w/c ratio (in initial amount of water) from the mix for post No. 3, 58 liters were discharged in comparison with 34 liters of sludge for post No. 5.

As expected, after 100 test cycles the strongest post was No. 3. However, even in this post, scaling of the mortar part of the concrete at the inner surface of the post was noted. The inner layers of concrete contain a relatively higher amount of water than the outer ones, this condition being caused by centrifuging. On post No. 5, destruction of this type proceeded to a depth of 20–25 mm. On all posts, except No. 3, at 100 cycles a network of longitudinal hair cracks appeared, with a smaller amount on post No. 4, the concrete of which contained a smaller amount of water in comparison with concrete posts Nos. 1, 2, and 5.

Extensive tests, performed with an industrial centrifugal machine in the laboratory shop of our Institute, have shown that during molding of posts by centrifuging it is possible to lower significantly the content of water in the concrete in comparison with the amount employed. Detailed instructions are given in the corresponding specifications for manufacture of centrifugal contact line posts. The importance of smooth changing of centrifugal speeds for compaction of the mix has been established.

The hardening regime, including steaming, is of exceptional importance for concrete durability.

Let us consider some of the results of our investigations of frost resistance of steamed concrete.

In 1955, the author began investigations on the influence of steaming on concrete manufactured from portland cement of high grade, and from rapid-hardening high-strength cements in particular. It was desired to establish the possibility of accelerating the process of manufacturing stressed reinforced products. Such investigations had never been performed previously. In various instructions on concrete steaming it has been mentioned that the lowest effect was that of steaming concrete made of portland cement (tables 7 and 8).

Several tests have been carried out for checking the frost resistance of steamed concrete on cement produced in vibratory mills. Cements "B" and "Bl" were used for making specimens of size 10×10×10 cm. The mineralogical content of cement "B" (in percentage) was C_3S, approximately 55 percent; C_2S, 20 percent; interstitial substance, 25 percent. The mineralogical content of cement "Bl": C_3S, 50 percent; C_2S, 20 percent; and interstitial substance, approximatley 25 percent. The specific surface (according to Derjagin) of initial cement "B" was 13,110 cm^2/g and of cement "Bl," 13,180 cm^2/g. After repeated grinding, the specific surfaces of the cements were 18,130 and 22,200 cm^2/g respectively. During repeated grinding no additives were introduced into the cement.

TABLE 7. *Influence of steaming regime on strength of concrete with portland cement "B"*

Item No.	Content of water in concrete	Ultimate compressive strength of concrete at various times							Steaming regimes				
		Normal hardening			After steaming				Duration of stages				Strength of sample in percentage of R_{28} of normal hardened sample
		3 days	7 days	28 days	1–2 days	3 days	7 days	28 days	Preliminary duration	Temperature increase to 80 °C	Duration at 80 °C	Temperature drop to 52–57 °C	
	kg/m³	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*hr*	*hr*	*hr*	*hr*	*Percent*
1	135	415	462	548	289	--------	482	558	--------	2	2	2 [a]	52.6
2	135	415	462	548	493	466	477	522	--------	3	2	10	89.5
3	135	415	462	548	433	--------	477	522	--------	2	2	10	80.5
4	135	418	462	540	494	--------	--------	--------	3	3	10	1 [a]	91.5
5	135	418	462	540	530	--------	--------	602	3	3	2	10	98
6	140	375	471	506	455	460	492	--------	--------	3	2	10	89.6
7	140	375	471	506	241	460	492	--------	--------	2	2	1 [a]	47.8
8	140	375	471	506	328	460	492	486	--------	2	2	1 [b]	64.8
9	150	466	467	534	442	416	464	484	--------	3	2	10	83
10	170	354	458	509	356	464	507	496	--------	3	2	10	70
11	190	278	357	375	268	338	339	390	--------	3	2	10	71.5

[a] The samples were removed from the steaming chamber at T=70–80° C.

[b] The samples were left for 15 hr in an open chamber. The concrete contained 450 kg/m³ of cement for each test series.

TABLE 8. *Influence of steaming regime on strength of portland cement "Bl"*

Item No.	Concrete components		Ultimate compressive strength of concrete at various times							Steaming regimes				
	Water	Cement	Normal hardening			After steaming				Duration of stages				Strength of sample in percentage of R_{28} of normal hardened sample
			3 days	7 days	28 days	1-2 hr	3 days	7 days	28 days	Preliminary duration	Temperature increase to 80 °C	Duration at 80 °C	Temperature drop to 52-57 °C	
	kg/m³	*kg/m³*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*hr*	*hr*	*hr*	*hr*	*Percent*
1	135	460	403	550	565	289	--------	468	535	--------	2	2	2 [a]	51.3
2	135	460	403	550	565	451	--------	468	535	--------	2	2	10	80.0
3	135	460	403	550	565	516	--------	409	564	--------	3	2	13	91.5
4	135	460	403	550	565	518	--------	499	544	--------	3	2	13	91.5
5	135	460	403	550	565	528	528	--------	525	3	3	2	12	93.5
6	135	460	403	550	565	491	--------	--------	519	3	3	10	2	87.0
7	150	450	--------	--------	527	450	--------	--------	502	--------	3	2	13	85.4
8	160	450	--------	--------	483	417	--------	--------	517	--------	3	2	13	86.4
9	170	450	--------	--------	427	343	--------	--------	510	--------	3	2	13	80.6
10	190	450	--------	--------	--------	220	--------	332	369	3	3	2	12	--------
11	190	450	--------	--------	--------	239	--------	--------	--------	3	3	10	2	--------

[a] The samples were removed from the steaming chamber at T=70–80 °C. The strengths of the steamed samples Nos. 2–6 are compared with the strength of sample No. 1, which experienced normal hardening.

The samples were made of concrete containing 450 kg of cement and 135 and 157.5 kg of water per cubic meter (w/c ratio–0.30 and 0.35).

Crushed granite was used as the coarse aggregate. Before steaming, the samples were stored for 3 to 5 hr. Both increase and decrease of temperature were carried out during 4 hr. Some of the samples were hardened under normal conditions.

Testing of samples for frost resistance was carried out in a freezing chamber. The samples were inspected after each cycle and were systematically weighed.

The hardening conditions play an important part in influencing the frost resistance of the concrete. If the hardening regime of concrete does not insure deep hardening, the frost resistance of the concrete is lowered. Similar destruction is observed in concrete hardening at the usual temperature with evaporation of water from it, and in concrete steamed at insufficient relative humidity.

The results of the tests show that concrete made with cement "Bl" was of lower frost resistance than concrete made with cement "B". This is clearly seen when testing specimens of concrete with high water content (157.5 kg/m^3). Whereas, for specimens made with cement "B", none of the investigated regimes of steaming significantly influenced frost resistance, the samples made with cement "Bl", with changed steaming regime and increase of temperature from 60 °C to 80 °C, and duration of isothermic heating of 12 hr, show sharply lowered frost resistance. The trend of lowered concrete frost resistance with cement "Bl" is shown also with specimens made with lower water content (135 kg/m^3), both for hardening under normal conditions and for steaming under various regimes. In both cases, a relatively low frost resistance was observed. Our numerous experiments with mortar and concrete samples, with synthetic (single-mineral and polymineral) cements, and with cements produced in laboratories and factories by grinding (the usual dry grinding, vibratory disintegration, and wet grinding), have shown that in several cases, the concrete (mortar) with a significantly lower cement content has an incomparably higher frost resistance. This fact, we consider, is connected in particular with increase in the cement of the active quantity of tricalcium aluminate, with its tendency to form coagulation structures that are not frost resistant. The introduction into the cement of plasticizers and an additional quantity of gypsum should lead to increase of the density of the reground cement and to increase of its frost resistance. However, at the present stage of investigation, not knowing the precise ratio of active quantities of gypsum and aluminate in the hardening process, we still cannot prove this beyond contradiction. The high frost resistance of concrete with cement "B" probably could be explained by the consideration that after its regrinding to a specific surface of 18,130 cm^2/g the ratio between the active amount of tricalcium aluminate and gypsum was more optimal (smaller amount of coagulation structure in the hardened cement paste), than in cement paste with cement "Bl", reground to a higher surface (22,200 cm^2/g). The above-mentioned conclusion is verified in particular by tests of the frost resistance of mortar specimens made with other kinds of cement from the same factories.

The tests performed have shown that steaming has a variable influence on the frost resistance of concretes of different compositions, manufactured from different cements.

The frost resistance of concrete manufactured from cement "B" and subjected to steaming by the mild regime, which insures obtaining a strength 73 percent of that of R_{28}, was not lower than the frost resistance of concrete hardening under normal conditions.

The testing of concrete manufactured from cement "Bl" has shown that its frost resistance depends on the water content. Concrete hardened under normal conditions, with a lower water content (135 kg/m^3), had a higher frost resistance. For concrete containing 157.5 kg/m^3 of water, the best results were obtained with samples steamed 16 hr at 60 °C. However, this concrete cannot be employed for products and structures subject to conditions of frequent and systematic freezing and thawing.

The conditions of concrete hardening influence to a very high degree the durability of the concrete. Therefore, when evaluating the rapid regimes of hardening of concrete it is necessary to determine the conditions of the hardening process (creation of structure) of the cement paste in the concrete.

The grade strength of the concrete is necessary as a criterion when estimating the conformance of design data to the actual strength of the concrete in the structure or product.

However, when estimating the quality of the concrete by the grade strength, in the majority of cases another technical-economic value of the same importance is forgotten—the relative strength of the concrete. The latter is directly connected with the degree of utilization or reaction of the cement in the process of concrete hardening up to 28 days. It is known that concrete of the same grade may be obtained with different kinds and grades of cement with significant degree of cement utilization. As a rule, after obtaining concrete of the required grade, the builder is not interested in further increase of concrete strength, just as the person designing the concrete composition is not interested in the problem of further increase of concrete strength, and in economy in relation to cement consumption. However, the increase of concrete strength, both during the first 28 days and for a longer time, is an objective indication of the quality of design, preparation, strength, and durability of the concrete.

Concrete, the strength of which increases systematically and with high intensity, will be of higher density and, consequently, of greater durability. If the concrete hardens for one day or for seven days under normal conditions, its strength after 28 days in both cases may be about the same, while the frost resistance will differ. This is natural and results from the simple determination after a long time of the strength of concrete specimens hardened under normal (100 percent relative humidity) conditions for a different time after preparation. Concrete hardening under normal conditions for 28 days continues to harden thereafter (naturally up to a certain limit). Concrete that hardens under normal conditions for only 7 days practically stops becoming stronger after 28 days. An even worse result is obtained in case the concrete hardens under normal conditions for less than 7 days. By grinding the cement and insuring normal conditions for concrete hardening, it is possible to lower the duration of the period of care (curing) of concrete and to increase its relative strength. In no case should the water be allowed to evaporate from the freshly placed concrete. If the steaming regime of concrete conforms to this condition and allows for full contraction in the cement paste, the latter is obtained with strong and durable structure, which simplifies and accelerates the technological process of manufacture of products. However, violation of the steaming regime is accompanied with intensive water evaporation from the concrete, leading to a low coefficient of utilization of the cement, lowering of relative strength and density of the concrete and, consequently, to lowering of durability.

Let us consider the results of testing the frost resistance of samples of plastic cement mortars (1:3) made with Volsk-type normal sand. The consistency of mortar mixes was similar in all cases. The mortars were made with portland cements "B" and "Bl". Cements produced at factories as well as those reground in vibratory disintegrators were used. Some lots of cement were reground with gypsum and plasticizers. The specific surface (according to Derjagin) of cement "B" produced in factories was 18,050 cm^2/g, and of cement "Bl", 14,730 cm^2/g.

As a rule, specimens with additives of gypsum and plasticizers came through the frost-resistance test with strengths nearly the same as those of corresponding specimens—standards—hardening in water.

The strength of specimens made without these additives was lower than that of the corresponding "standard" specimens.

The tests showed that, with one and the same cement, it is possible to obtain mortars possessing different frost resistances. They also verified the influence of the fineness on the lowering of frost resistance, when not combined with organized direct hardening of the cement paste.

Thus, for example, specimens made with cement containing an additive of 3 percent gypsum and 0.2 percent sulfite cellulose extract, and having a specific surface of 21,050 cm^2/g, reached after 300 test cycles a strength of 557 kg/cm^2, while the corresponding "standards" showed 678 kg/cm^2.

Specimens made with cement not containing additives, and having a specific surface of 25,260 cm^2/g, already after 250 cycles had lower strength in comparison with the "standard." The latter had a significantly lower strength than the specimens made with coarsely ground cement but containing additives. As a result of repeated grinding in vibratory mills three lots of each cement were obtained differing in degree of fineness. The specific surfaces of the different lots of cement "B" were 15,730, 13,130, and 20,330 cm^2/g; of cement "Bl", 18,600, 21,050, and 25,260 cm^2/g (tables 9 and 10).

The specimens of cement mortars were first tested for frost resistance in a freezing chamber and then at climatic station No. 2, where they passed 50 to 200 freezing-thawing cycles. At the same time that the strength of the specimens that had frozen was being determined, corresponding specimens stored in water under normal conditions were tested. Testing of the specimens was stopped after the edges and corners became rounded (rating point 3). During testing of samples in compression, scattering of results was observed, this being explained by the imperfection of the test procedure. In several cases lowered strengths were obtained owing to the distorting influence, in the press, of the destroyed surface layer of the cement mortar, even though as a whole the test specimen was not destroyed.

In the specimens that were under the action of aggressive media, it was necessary, before the compression test, to determine the hardness of the surface layers, in order to avoid the influence of the latter on the strength. It was also necessary to polish the surface of the sample prior to compression testing, in order to create comparable conditions for testing.

Hardening of concrete under conditions hampering the hydrolysis and hydration processes of cement reduces the quality and leaves a remainder of unreacted cement. It is incorrect to solve the problem of correct content of cement, and manufacture of durable concrete, by fine grinding of the cement, by vibration of the concrete mix at different frequencies, etc., without taking into account the importance of self-compaction of the concrete during the hardening process. This problem has seldom been considered in the technical literature.

Curing of structures of precast reinforced concrete is of very great importance, since their cross sections are small. Lately, in the technical literature, an outstanding problem has been the durability (strength) of concrete and the role of protective layers over the reinforcement, which is also connected with the use of precast structures. The mechanical strength of concrete is referred to as "stability," in order to accentuate the possibility of its impairment as time passes. However, these articles do not consider the importance of the conditions and time of hardening of concrete, plain

TABLE 9. *Frost resistance of plastic mortars (1 : 3) of portland cement "Bl"*

Item No.	Specific surface of cement	Additive		w/c ratio	Compressive strength of sample							
		Sulfite cellulose extract	Gypsum		After the indicated number of test cycles [a, c]							At climatic station additionally after 50 to 200 test cycles
					100	150	200	250	300	350	400	
	cm²/g	*Percent*	*Percent*		*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1 [b]	13,050	------	------	0.5	$\frac{200}{308}$	$\frac{249}{383}$	$\frac{201}{362}$	$\frac{203}{494}$	$\frac{245}{390}$	$\frac{270}{449}$	$\frac{293}{473}$	$\frac{218}{429}$
2 [b]	15,730	------	------	.5	$\frac{300}{382}$	$\frac{185}{385}$	$\frac{177}{377}$	$\frac{171}{381}$	$\frac{224}{450}$			$\frac{218}{429}$
3	15,730	0.2	3	.37	$\frac{413}{410}$	$\frac{403}{425}$	$\frac{390}{455}$	$\frac{314}{436}$	$\frac{368}{500}$	$\frac{395}{508}$	$\frac{449}{488}$	$\frac{420}{498}$
4	15,730	.2	5	.4	$\frac{300}{278}$	$\frac{310}{392}$	$\frac{362}{430}$	$\frac{334}{438}$	$\frac{425}{498}$			$\frac{450}{439}$
5	18,130	------	------	.5	$\frac{285}{371}$	$\frac{204}{374}$	$\frac{220}{390}$	$\frac{217}{422}$	$\frac{77}{424}$			$\frac{222}{390}$
6	18,130	.2	3	.4	$\frac{424}{444}$	$\frac{355}{415}$	$\frac{332}{431}$	$\frac{422}{527}$	$\frac{364}{455}$	$\frac{493}{551}$		$\frac{430}{469}$
7	18,130	.2	5	.4	$\frac{401}{436}$	$\frac{300}{367}$	$\frac{379}{370}$	$\frac{316}{523}$	$\frac{382}{406}$	$\frac{429}{508}$		$\frac{429}{449}$
8 [b]	20,330	------	------	.5	$\frac{148}{410}$	$\frac{222}{450}$	$\frac{205}{484}$	$\frac{---}{444}$				$\frac{257}{410}$
9	20,330	.2	3	.4	$\frac{450}{460}$	$\frac{392}{488}$	$\frac{363}{535}$	$\frac{481}{541}$	$\frac{522}{537}$	$\frac{493}{527}$	$\frac{444}{552}$	$\frac{498}{527}$
10	20.330	.2	5	.45	$\frac{435}{420}$	$\frac{303}{480}$	$\frac{369}{337}$	$\frac{300}{284}$	$\frac{305}{367}$	$\frac{434}{498}$		$\frac{459}{596}$

[a] The value above the line shows the strength of the specimens after freezing, the value below the line shows the strength of specimens hardened in water at normal temperature.

[b] Testing of part of the specimens was stopped, as some were rated at point 3.

[c] The maximum values of strength are indicated.

and reinforced. Several Soviet and foreign authors have carried out interesting investigations in this field. In our book "Concrete Durability," it was shown that to obtain durable concrete it would be necessary to insure its hardening in a moist condition for at least 90 days (p. 338, table 130). In one interesting theoretical work by Powers, the conditions were considered under which the processes of cement hardening proceed with different intensity. However, due to the fact that this problem is very complex, a simple and expedient solution for construction purposes has not as yet been evolved. It is possible to agree with the view of Powers on the inadmissibility of water evaporation from the capillaries of the cement paste as, in this case, cement hydration stops, this being verified by our experiments and by lowering of the engineering properties of the concrete. Powers indicates that previously it was considered possible to allow evaporation of part of the water from the cement paste, due to the excessive amount of water in the concrete in comparison with the amount needed for the hardening process. At present, it is considered that cement hydration may proceed completely and at a high rate (at required temperatures) only in case the concrete or cement paste is completely saturated with water. We cite these opinions in order to emphasize the insufficient number of investigations devoted to this problem, which is, after all, decisive for the quality of concrete and reinforced concrete. Aside from the problem of migration of moisture in concrete, at the given stage of investigation it is possible to assume that the water introduced into the concrete should be available along with the cement for the required new formation, without evaporation.

The possibility of cement hardening, and of obtaining a material of the required grade of strength under practically any conditions, is dependent on the presence in the concrete of a sufficient quantity of fine cement fractions and of surplus water. However, in this case, the hardening process proceeds selectively. Such concrete, after some time, stops becoming stronger and it is not durable in aggressive media. Unfortunately, there are no detailed and systematic experiments on investigation of the influence of the hardening regime on the engineering properties of concrete made with different binding materials. One of the indications of the influence of hardening conditions, and, consequently, the degree of cement hydrolysis and hydration, may be change of the water permeability of concrete made with portland cement. In 1939 we had already performed several experiments. Water permeability of con-

TABLE 10. *Frost resistance of plastic mortars (1 : 3) of portland cement "B"*

Item No.	Specific surface of cement	Additive		w/c ratio	Ultimate compressive strength of sample									
		Sulfite cellulose extract	Gypsum		After the indicated number of test cycles [a], [c]									At climatic station additionally after 50 to 200 test cycles
					100	150	200	250	300	350	400	450	500	
	cm²/g	*Percent*	*Percent*		*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	14,730	----------	----------	0. 5	$\frac{320}{385}$	$\frac{283}{380}$	$\frac{229}{319}$	$\frac{84}{354}$						$\frac{260}{430}$
2	18,600	----------	----------	. 55	$\frac{310}{410}$	$\frac{253}{382}$	$\frac{251}{258}$	$\frac{119}{506}$	$\frac{80}{375}$					$\frac{381}{449}$
3	18,600	0. 2	3	. 42	$\frac{296}{462}$	$\frac{425}{535}$	$\frac{354}{582}$	$\frac{415}{542}$	$\frac{459}{576}$	$\frac{424}{571}$	$\frac{371}{517}$			$\frac{449}{489}$
4	18,600	. 2	5	. 39	$\frac{266}{437}$	$\frac{342}{485}$	$\frac{297}{532}$	$\frac{353}{560}$	$\frac{404}{542}$	$\frac{430}{545}$				$\frac{410}{508}$
5 [b]	21,050	----------	----------	. 5	$\frac{349}{470}$	$\frac{385}{445}$	$\frac{256}{422}$	$\frac{279}{559}$						$\frac{280}{518}$
6	21,050	. 2	3	. 4	$\frac{495}{455}$	$\frac{465}{555}$	$\frac{402}{485}$	$\frac{473}{542}$	$\frac{557}{678}$					$\frac{488}{576}$
7 [b]	25,260	----------	----------	. 53	$\frac{269}{419}$	$\frac{150}{405}$	$\frac{174}{507}$	$\frac{161}{400}$						$\frac{208}{449}$
8	25,260	. 2	3	. 46	$\frac{347}{430}$	$\frac{502}{599}$	$\frac{485}{512}$	$\frac{362}{477}$	$\frac{405}{537}$	$\frac{468}{610}$				$\frac{226}{518}$
9	25,260	. 2	5	. 5						$\frac{449}{432}$	$\frac{425}{532}$	$\frac{426}{503}$	$\frac{337}{488}$	$\frac{296}{469}$

[a] The value above the line shows the strength of the specimens after freezing; the value below the line shows the strength of specimens hardened in water at normal temperature.

[b] Testing of part of the specimens was stopped, as some were rated at point 3.

[c] The maximum values of strength are indicated.

crete made of low-aluminate cement and hardened in air was investigated at different ages. The amount of cement in the concrete was 250, 300, and 350, and of the water, 175 kg/m³. The ultimate compressive strength of the concrete was 260 to 440 kg/cm². Specimens tested after 80 days under a pressure of 5 atm, had a coefficient of permeability of $(0.110–0.300) \cdot 10^{-7}$. The same specimens, as well as control specimens, were tested after 230 days under the same pressure. It was found that the coefficient of permeability increased up to $(22.4–41.2) \cdot 10^{-7}$. These experiments may serve as obvious proof of the change proceeding in the cement paste and, in particular, in the gel component during evaporation of water from it with time. It is necessary to avoid the possibility of such changes by creating the appropriate hardening conditions. From this point of view we propose to consider the technological methods of operation, and acceleration of concrete hardening.

Given below are the final tabulated results of long-time testing at the climatic station of 20-cm. concrete cube specimens, made of cement from "K" clinker, ground in the CM–14 mill. Sulfite cellulose extract was added to the clinker during grinding. After 7 years of testing (5,000 cycles) the condition of the samples was estimated by rating point 9. In the majority of cases duplicate samples differed insignificantly from each other. For each composition 9 to 12 cubes were tested; 6 to 7 years of testing were passed without destruction by 25 lots of samples (table 11).

TABLE 11. *Characteristics of concrete resisting about 5,000 freezing-thawing cycles in situ*

Item No.	Concrete components		w/c ratio	Sulfite cellulose extract additive	Estimation of samples by rating points after the indicated number of years of testing					
	Water	Cement			1 yr	2 yr	3 yr	4 yr	5 yr	7 yr (5,000 cycles)
	kg/m³	*kg/m³*		*Percent*						
1	145	290	0. 5	0. 2	10–9	10–9	10–9	10–9	10–9	9–8
2	146	265	. 55	. 2	10–9	10–9	10–9	10–9	10–9	9–8
3	147	226	. 65	. 2	8	7–6	7–2	------	------	6–0
4	148	212	. 7	. 2	6	6–5	4–2	------	------	-------
5	145	290	. 5	. 1	10	10–9	10–9	10–9	10–9	9–7
6	153	280	. 55	. 2	10–9	10–9	10–9	10–9	10–9	9–8

Testing of prestressed reinforced sleepers for frost resistance also verified the significant influence of the steaming regime on the durability of products and structures. The concrete contained 450 kg/m³ of cement and 145 kg/m³ of water. Some of the sleepers were steamed in pit chambers at a regime of 6+3+10+5 hr., and the rest were placed below a wooden hood, with leaking of part of the steam. After 100 test cycles the influence of the hardening regime on frost resistance was already detected. After 300 cycles the sleepers steamed under the hood were seriously deteriorated.

Principles of Designing Durable Concrete

Besides selecting the concrete components, according to the grade given in the project, it is also necessary to design the concrete mix in such a way that it conforms with other technical requirements.

The grade of durable concrete is understood to be the ultimate strength reached by the concrete in the structure after the designated life under actual ambient conditions, the aggressive action of which is determined during design of the structure and is taken into account in the design of the concrete. When designating the grade of durable concrete, the construction methods should be taken into account; namely, time of finishing the structure or part of it and loading with design forces; season of the year and climatic conditions when the concrete mix is being placed and the concrete hardens in the structure; massive or openwork type of the structure, construction methods, and type of reinforcement—common or prestressed. This is the first design stage.

The second stage of concrete design is the selection of materials for the concrete, the selection of the concrete composition, and its testing. There are some features distinguishing this work. At present, when selecting the components of concrete, only the ultimate strength of a laboratory specimen is considered without estimating the ultimate strength of the same specimen after it has been under the action of external aggressive influences. The author proposes a different principle of selection of the components of the concrete, consisting in selection based on the ultimate strength of a specimen hardened under conditions modeling in the laboratory the entire term and conditions of use of the concrete after erection of the structure. At present, when selecting the components of concrete for cases when, besides the grade, it is necessary to establish the fitness of the concrete for exposure to different aggressive media or to the action of different loads, estimation of the stability of the concrete specimen is accomplished not by testing it until it is destroyed, but up to some conditional limit.

In no case is the limit value of the load and time known, when the tested concrete is destroyed. This is true whether using concrete with insufficient or excessive stability against the action of the actual exposure after the structure has been erected.

The disadvantages of concrete under the action of ambient influences do not become apparent at once, but only after decades have passed. Unfortunately, in these cases, selective, periodic inspection of concrete does not allow of obtaining material for analysis of the causes of detected defects.

Conclusions

1. Of decisive importance for best results from use of cement in construction is the classification of the latter by the indications determining long-time behavior of the cement paste in the structure under various conditions of exposure and use. Though the conditions of use of the cement mortar or concrete vary, they may be and are necessarily estimated when certifying the cement for one or another structure. All of this may be accomplished by properly working out the cement mortar and concrete classification for producing cement at the site with properties corresponding to the working conditions, thus guaranteeing the quality indicated in the certificate, and by correct performance of concreting operations.

2. As the basis for using cement, the new classification should be adopted, taking into account the following:

(a) lack of waterproof capacity and, consequently, lack of frost resistance of hydrated tricalcium aluminate, hydrosulfoaluminate, and hydrated tetracalcium aluminoferrite;

(b) slow belite hardening;

(c) properties of active mineral additives for portland cement to increase impermeability and sulfate resistance of concrete and which affect its frost resistance;

(d) features of mono- and multi-component cement that make it impossible to obtain concrete of high frost resistance;

(e) the possibility of improving some of the building properties of cement by introducing plasticizers and air-entraining additives, and some new views and premises on the basis of investigations in this field.

3. When working out the new classification of cements having, as its aim, use in various structures of the most durable materials, the author proposes to use the principle of directed structure formation. The basis of correct use of this method is the consideration of actual properties of poly-mineral cement. The reaction processes should be the main part of the processes connected with the formation of the hardened cement paste and should be directed in the hardened material.

4. Thorough solution of the problem of durability of plain concrete and reinforced concrete will help to improve planning, distribution, and manufacture and delivery of cement, this solution being very important for obtaining concrete of much higher quality with lower cement content.

5. It is known that there is a widespread point of view that even in those cases where the cement does not conform in its properties to the actual conditions under which it is to be placed in the concrete, increase of cement content and corresponding lowering of the w/c ratio make it possible to obtain concrete of the required quality. In-

crease of the quantity of cement in laboratory tests shows increase of strength and some increase of stability of the samples, for example when testing them for frost resistance, but that is all. Practically, non-conformance of cement with external aggressive conditions is not overcome.

6. The use during scientific investigations of cement prepared according to new technology has led to several new solutions in relation to correcting some of the disadvantages of cement, cement with a high alumina modulus, for example. The idea of sulfate-resistant cement is a case in point. The same relates to the problem of obtaining mortars and cement with smaller shrinkage, expanding cement, and concrete with higher frost resistance in comparison with concrete of the same cements obtained in the usual way.

7. The main cause of insufficient introduction into production of the achievements of investigators in the field of technology of cement and concrete consists in the fact that these achievements are insufficiently reflected in the main technical documents—construction standards and specifications.

8. Correct estimation of the workability of the mix, and its design for application to actual conditions is of decisive importance for the progress of concrete work, and for obtaining structural concrete with the given technical characteristics (impermeability, frost resistance, etc.).

9. The formation of frost-resistant structures is directly connected, first of all, with use of the effect of contraction. Air is a required component of the cement paste, serving as a damper in the spaces formed during hydration of the cement minerals.

10. With frost-resistant coarse aggregate and unchanged concrete structure the hardened cement paste determines the stability of the concrete. The cement paste cannot improve the frost resistance if the rock material is not itself resistant to repeated freezing-thawing cycles.

11. Depending on which materials were chosen and on how well the plain concrete or reinforced concrete was prepared for the given grade of structure, the prevailing external influences may gradually destroy the concrete or may not have any aggressive action upon it.

12. When the proper conditions of mortar or concrete hardening are not observed in the structures their durability becomes uncertain.

13. It should be borne in mind that proper arrangement, in the structure, of prestressed reinforcement is essential and sometimes decisive for reliable behavior of reinforced concrete under the action of repeated alternating freezing and thawing.

14. Selection of the thickness of the protective layer should be determined not only by frost resistance, but mainly by the time of preservation, near the reinforcement, of an alkaline medium.

SESSION VII. CHEMICAL ADDITIONS AND ADMIXTURES

Paper VII-1. Some Chemical Additions and Admixtures in Cement Paste and Concrete*

H. E. Vivian

Synopsis

Important problems are encountered in the behavior of available cements and aggregates, in handling freshly mixed concretes and grouts, and in the properties of hardened concretes in various types of structures exposed to all types and combinations of weathering conditions. Any admixture or technique that can assist in overcoming these problems, without introducing further serious defects, has a useful place in concrete technology. It is not intended to advocate that admixtures should be used in all concrete or should eliminate the need for suitable mix design, handling techniques, or control of constructional operations; rather they should be used to counteract specific defects or problems and to confer additional advantages that will permit concrete to be used successfully or will assist concrete to carry out its designed function.

Chemical admixtures, which are usually added in relatively small quantities and generally interact chemically or physically with cement paste, are designed to affect a wide variety of paste and concrete properties. They may be used to vary setting times and rates of strength gain in order to meet particular construction requirements. Similarly the workability of freshly mixed concrete may be modified to meet specific construction requirements or methods or to produce specific types of products. It is in connection with improvement in durability that admixtures have been particularly useful. Entrainment of air in concrete is rightly regarded as a major factor in improved durability while attention is directed towards the new admixture field of inhibition of steel-reinforcement corrosion. Surface treatments which, although not strictly admixtures, are often closely allied in their action to waterproofers, may also modify concrete behavior and improve its durability.

On account of the lack of necessary basic data on the reactions that can occur in cement paste and on the mechanisms by which its physical properties develop, it is impossible to describe with certainty the various behavior mechanisms of many admixtures. Available data indicate that the major concrete problems are concerned with such properties as low tensile strength, volume instability, and cracking and durability. Further studies of the causes of these inadequacies and the development of techniques and admixtures for their improvement are clearly indicated.

Résumé

Le comportement des ciments et aggrégats disponibles, la manipulation des bétons et des coulis injectés, et les propriétés des bétons durcis dans différents genres de constructions exposées aux conditions atmosphériques les plus variées, présentent d'importants problèmes. Tout produit d'addition ou toute méthode qui peut contribuer à surmonter ces problèmes, sans introduire de sérieuses imperfections supplémentaires, a une place utile dans la technologie du béton. Il n'est pas dans l'intention de l'auteur de préconiser l'emploi des produits d'addition dans tous les bétons, ni d'affirmer qu'ils rendent inutiles la détermination des proportions du mélange, les méthodes de manipulation ou le contrôle des opérations de construction; leur emploi devrait plutôt avoir pour but de neutraliser certains défauts ou problèmes spécifiques et de conférer des avantages supplémentaires qui permettront d'utiliser le béton avec succès ou aideront le béton à remplir les fonctions qui lui sont dévolues.

Les produits d'addition chimiques, qui sont généralement ajoutés en quantités relativement petites et réagissent chimiquement ou physiquement avec la pâte de ciment, ont pour but d'affecter un grand nombre de propriétés diverses de la pâte et du béton. On peut les utiliser pour varier les durées de prise et les vitesses de l'accroissement de la résistance afin de satisfaire aux exigences de construction particulière. De la même façon la maniabilité du béton fraîchement malaxé peut être modifiée pour répondre aux exigences ou aux méthodes de construction spécifique, ou pour produire des produits spécifiques. Les produits d'addition ont été particulièrement utiles en ce qui concerne l'amélioration de la durabilité. On considère que l'entraînement d'air dans le béton est considéré à juste titre un facteur de première importance dans l'amélioration de la durabilité, tandis que l'attention est dirigée vers les nouvelles méthodes d'utilisation des produits d'addition pour empêcher la corrosion de l'armature en acier. Bien qu'on ne puisse les considérer comme des produits d'addition à proprement parler, les traitements de surface sont souvent très proches par leur action des imperméabilisateurs, et peuvent également modifier le comportement du béton et améliorer sa durabilité.

Par suite du manque de résultats fondamentaux nécessaires sur les réactions qui peuvent se produire dans la pâte de ciment et sur les mécanismes suivant lesquels ses propriétés physiques se développent, il est impossible de décrire avec exactitude les mécanismes variés du comportement de nombreux produits d'addition. Les résultats disponibles indiquent

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que les principaux problèmes du béton ont rapport aux propriétés telles que la basse résistance à la traction, l'instabilité volumétrique, la fissuration et la durabilité. Les études à poursuivre sur les causes de ces imperfections et le développement des méthodes et produits d'addition dans le but de les améliorer sont clairement indiquées.

Zusammenfassung

Bedeutende Probleme des Verhaltens der bekannten Zemente und der Zuschlagstoffe, der Behandlung frisch gemischter Betone und Mörtelschlämme und der Eigenschaften des gehärteten Betons in allen Konstruktionen, die den verschiedensten Arten von Wetter und Klima ausgesetzt sind, müssen noch gelöst werden. Irgendeine Beimischung oder Behandlung, die ein Problem löst und keine neue schlechte Eigenschaft hervorruft, wird in der Betontechnologie willkommen geheißen. Das muß nun nicht so verstanden werden, daß man in allen Betonen irgendwelche Beimischungen einverleiben und dann die Art und Weise der Mischung, die Verarbeitung und die Überwachung der Baukonstruktion vernachlässigen soll; nein, man soll Beimischungen nur für das Berichtigen bekannter Fehler benutzen, und um neue, bessere Eigenschaften hervorzubringen, damit der Beton dann mit vollster Zufriedenheit benutzt werden oder daß man wenigstens seine Benutzung anziehlicher machen kann.

Chemische Beimischungen, die meistens in kleinen Mengen hinzugefügt werden, und welche im allgemeinen mit der Zementpaste chemisch oder physikalisch reagieren, sollen mehrere Pasten- und Betoneigenschaften gleichzeitig verbessern. Sie können zum Beispiel für die Veränderung der Erstarrungszeiten oder Festigkeitszunahme zugegeben werden, sodaß man den Zement für Spezialkonstruktionen benutzen kann. In der gleichen Art und Weise kann man die Verarbeitbarkeit frischen Betons beeinflussen, sodaß dieser dann in Spezialkonstruktionen, für bestimmte Bauweisen oder für Spezialprodukte benutzt werden kann. Die Dauerhaftigkeit ist durch solche Beimischungen ganz besonders günstig beeinflußt worden. Man hat schon ganz richtig erkannt, daß ein hoher Luftgehalt im Zement die Dauerhaftigkeit sehr günstig beeinflußt, aber man schenkt das Augenmerk jetzt einigen neuen Beimischungen, die die Korrosion der Stahleinlagen verhindern sollen. Oberflächenbehandlungen sind genaugenommen keine Beimischungen, aber sie haben doch eine ähnliche Wirkung wie wasserabstoßende Mittel, daher können sie das Betonverhalten beeinflussen und die Betonbeständigkeit verbessern.

Da man die Reaktionen, die in der Zementpaste stattfinden können, noch nicht genau kennt, und da man nichts über den Mechanismus, der zur Entwicklung der physikalischen Eigenschaften führt, weiß, kann man nicht zu genau die Gründe beschreiben, warum diese oder solche Beimischungen diesen oder jenen günstigen Effekt hervorrufen. Von den Literaturangaben kann man herleiten, daß die Beimischungen meistens zur Verbesserung einer niedrigen Zugfestigkeit, mangelhafter Raumbeständigkeit, der Rißbildung und der Dauerhaftigkeit verwendet werden. Man muß daher die Gründe dieser Nachteile noch mehr erforschen und Verfahrensweisen und Beimischungen, die solche Nachtele überkommen sollen, entwickeln.

Introduction

The literature in the field of concrete admixtures is studded with specific instances of why some modification of concrete was necessary, certain claims that beneficial effects could be obtained with certain addition materials, discussions of the changes produced under different working or environmental conditions, and compilations of rules and recommendations for their use. A very useful summary of types of admixture materials, their purposes and rules for their use has been published by the American Concrete Institute Committee 212 [1][1]. These published data are pertinent to the study and application of chemical additives and admixtures, and in addition the properties, uses, and effects of the more bulky admixtures (e.g., pozzolan and blast-furnace slag) have received considerable attention. Consequently it is intended that the present discussion should be confined to the effects produced by those admixture materials that are added in minor quantities to cement paste and concrete and will not include more than passing comment on economic or technological factors that naturally arise when large-scale use is attempted. Other papers to be presented at this Symposium are concerned specifically with the bulkier admixture materials, with false setting and the early hydration reactions, and with the properties of hardened paste and concrete. So as to avoid repetition, comment within these fields will be kept to a minimum.

To plan and carry out useful research on the use of admixtures in concrete it is necessary to recognize and assess the various problems that occur in cement paste and concrete as materials, that occur in the materials when handled in specific ways, or that occur in finished products or structures which are subjected to various environmental or operational conditions. It is clearly necessary therefore to inquire into the chemical and physical actions that admixtures impress on cement paste and concrete at all stages from the initial mixing until the useful life of a structure has ended.

As a beginning it would be desirable to examine briefly the faults and defects that appear to be inherent in cement-paste and concrete systems. With an understanding of the modifications required, it is possible to study the actions of some types of additives and to assess whether their effects are satisfactory in overcoming the defects without introducing further problems.

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[1] Figures in brackets indicate the literature references at the end of this paper.

A discussion such as this also offers an opportunity for comment on possible future developments. Improvement in the intrinsic strength of hydrated cement and reduction in the importance of the allied problems, drying shrinkage and cracking are of great importance. Bond between cement paste and aggregate and between cement paste and reinforcement is being studied in order to improve structure performance. Methods by which concrete is rendered less easily penetrated by moisture or solutions should increase its stability and durability. Great importance is attached to possible future developments. Although it can be truly said that, while the properties of cement paste and concrete can be adapted and improved to meet the needs of today, the new uses to which concrete will be put tomorrow will place still greater demands on improved materials, properties and techniques.

Admixtures may be regarded as materials, other than the normally accepted ingredients of concrete, that are added to the mix immediately prior to or during mixing. There are certain treatments which, according to definition, are not admixtures. When applied to hardened concrete surfaces however, they may interact chemically or physically with the hydrated cement and induce effects that are similar to those of typical admixtures. It is considered justifiable therefore to make brief mention of some of the more useful of these surface treatments.

Hydrated Cement Paste and Concrete

Hydrating cement may be regarded as a dynamic system that has certain specific requirements, that may differ at different times in its history. These requirements may not be needed before a certain stage is reached or they may not be needed after a certain stage has passed. The effects induced however by a preceding action or treatment may be decisive in determining the later behavior of the concrete.

Cement paste and concrete, when freshly mixed, may be regarded as concentrated suspensions, which behave differently from dilute suspensions, because the paste is flocculated and cohesive. Powers [3] and Steinour [4] in their studies on the "bleeding" of cement paste postulated that it tended to behave as one large floc. On standing, the solids sediment and water "bleeds" at a rate that depends on its ease of escape from the paste. There may be considerable segregation within the sedimented-solids bed. These tendencies are, of course, carried forward and perpetuated in the hardened concrete. Workabliity, which is a very transitory requirement of any concrete mix, represents the ease with which the mass can be moved, deformed in shape, and compacted without its constituents undergoing separation or segregation. The resultant effects of the interaction between the concrete-mix properties and the method of placing, are "frozen" into the hardened concrete. Other minor effects, such as premature stiffening or false set, may also modify some of the desirable properties of cement paste and concrete and consequently either render normal placing techniques unsuitable or require the development of new equipment or methods.

The variability of cement, aggregates, and mixes as well as the multitudinous differences in types of work, methods of construction, and handling equipment have all accentuated the problems associated with freshly mixed cement paste or concrete. In many instances admixtures have been used to overcome specific difficulties, and a few types of operations may be quoted to illustrate the breadth of their potential use. The properties of the cement paste or concrete are generally modified by additives to permit pumping as grouts, linings for oil wells, or as linings for tunnels. Placing as a lining in pipes, on slopes for slip-forming, as pneumatically applied mortar, placing in narrow, heavily reinforced sections in contrast to open, unreinforced or lightly reinforced sections, have different requirements in regard to concrete properties, and these may sometimes be achieved more readily or effectively by the use of additives. It should be noted that the use of admixtures does not eliminate the need for designing the most suitable concrete mix with the available materials.

Hydration of cement is not an instantaneous process but occurs over a very long period of time during which chemical and physical changes occur within the mass. These changes depend to some extent on the environmental conditions to which the mass is subjected. The change from what may be regarded as a suspension of solid particles dispersed in water, which constitutes the continuous phase, to a solid mass in which water becomes the disperse phase, is a major one. It induces numerous problems mainly concerned with volume changes and strength development, starting from the time when stiffening commences, and remaining operative when hard set occurs and afterwards, since the hydration reactions proceed for a considerable time after the final set occurs. Such actions as drying shrinkage applied to a hardened mass of concrete that may be regarded as being rigid (within the short time scale usually employed) and of limited elasticity, must induce the development of numbers of cracks in positions of stress concentration. The basic questions about strength still remain unanswered. How strength is developed is unknown, the actual properties of the hydrated products and their associations are unknown, and the complex interactions of the chemical and physical actions are unknown. In short very little is known about the characteristics that confer strength and the way in which it is developed. Little more is known about the properties of clinker, especially its uniformity of behavior and whether cements produced from it can be made to act more effectively. It will be readily seen that when admixtures are studied in relation to these complex and largely unknown processes the results are generally confused and often not helpful. For these reasons the amount of work that has been done on the effects of admixtures on cement hydration and strength development has been limited. The more obvious and more easily measured changes in acceleration and retardation of setting and strength gain have been studied, but even in this more limited field the actions of the admixtures are incompletely understood.

The effect on sound concrete of environmental conditions is usually of paramount importance since they affect both the short term behavior of fresh concrete and the long term behavior of hardened concrete. Much emphasis has been rightly placed on the need for improved durability, and various additives have been used in attempts to achieve this end result. Undesirable properties such as low strength, excess mixing water, shrinkage stressing and cracking, and low bond between cement paste and aggregate and between mortar and reinforcement cause structure deficiencies and may lead to low durability. Under specific conditions of use or exposure, certain problems may become all important in their effects on concrete durability. Examples which may be given briefly include: (1) settlement of fresh concrete under large aggregate, under reinforcement, and in back-filling inverts which may cause lack of bond, with consequent reduction in mechanical properties, and increased permeability to water; (2) loss of workability in pumped concrete and grout, which interrupts the construction schedule and reduces compaction and strength as well as increases permeability; (3) volume changes in hardened concrete, which cause strength reduction or disruption (these volume changes being due to reactive aggregates, reinforcement corrosion, frost action, or aggressive salt action); and (4) abrasion resistance which is necessary to combat mechanical damage to surfaces. There are undoubtedly many more examples of special cases of concrete, under certain specific environmental conditions, either failing or giving an inadequate performance to meet the required demands. The use of admixtures, which are designed to assist the performance of concrete under the imposed conditions, will be discussed later.

Finally it would be desirable to note a few of the properties of cement paste and concrete that at present must be accepted as inevitable since they cannot be prevented. Engineering design will usually minimize the incidence of these effects as far as the structure is concerned; the chemical and physical effects on the material itself however remain unaffected. Some of these effects are discussed below.

Since the hydration reactions are exothermic, the accumulation of heat within a concrete mass makes curing extremely difficult or impossible to achieve ideally. The heat gradient in the mass regardless of curing tends to redistribute water within the concrete mass and between the concrete and the surrounding atmosphere. These effects together with differential thermal expansion in different parts of a structure may cause considerable volume changes.

Volume changes within the cement paste itself as a result of the hydration reactions and of drying shrinkage are inevitable. They occur largely after the concrete has hardened and become rigid, and consequent stressing causes cracks to develop. Changes in external dimensions, due to plastic deformation under applied stress, or "creep," are due to independent movement of different portions of the mass. The exact nature of creep in concrete has never been fully explained.

The hydration reactions of the various clinker minerals as well as other chemical interactions may proceed for a very long period of time. Moreover the hydrated clinker compounds appear to be capable of undergoing modification depending on their environmental conditions. These reactions are not all beneficial, and those tending to accentuate the unstable tendencies of hydrated cement, when taken to extremes, are detrimental to physical properties.

The particulate nature of hydrated cement which implies a certain amount of internal pore space, that may be filled by gas or liquid, induces a number of permeability problems associated with specific environmental conditions. These problems may sometimes be countered by the use of densifying admixtures or by surface treatments to reduce surface permeability.

Although it is not possible to deal with all the possible admixtures under all the possible conditions of exposure, it will be seen that there is ample scope for the use of admixture materials that confer specific properties on concrete. It is necessary to insure that these properties are adequate to overcome the effects induced by the environment and that in producing them other deleterious effects are not being introduced. With these background problems and requirements in mind, a discussion of certain types of admixtures and their effects in cement paste and concrete will now be attempted.

Admixture Actions

Admixtures added to concrete in small amounts may be classified very briefly according to the type of action that they produce. They may be described as:

1. Retarders or accelerators of hydration or other chemical reactions and of strength development.
2. Workability aids in freshly mixed pastes and concretes.
3. Surface-active agents and other materials that entrain air or act as waterproofers.
4. Corrosion inhibitors.
5. Miscellaneous admixtures.

Retarders or Accelerators of Hydration or Other Chemical Reactions and of Setting and Hardening

Little more than a few brief comments on the action of accelerators and retarders in cement and concrete can be given here. Steinour [2] in his review on the setting of portland cement has collected and arranged a vast amount of data, and this should serve as a basis on which future discussions and work can be planned. The introduction of other problems such as premature stiffening and "false" set need not be attempted here since these problems are the subject of a separate paper.

It is necessary however to point out that cement as normally used (i.e., as a mixture of ground clinker and gypsum) has generally undergone considerable modification when viewed against the behavior of the ground clinker alone. Gypsum may act with some clinkers and under some conditions as a retarder, whereas under other conditions and with the same or other clinker it may act as an accelerator. This lack of a consistent behavior pattern has been the main cause of the present confusion in connection with setting behavior of cements and with an overall mechanism to describe it. The subject is a difficult one on account of the large number of possible reactions that could occur either simultaneously or consecutively. When these reactions are complicated further by the addition of another admixture material, that either accelerates or retards the setting behavior, which may be regarded as normal, a completely new set of reactions may be induced or the admixture may accentuate one or more of the normal reactions or it may counteract one or more of the normal reactions. A short description of what is thought to happen may illustrate this point.

Finely ground clinker (without gypsum) may be either quick or slow setting. Although the causes of this difference in behavior are still obscure, it is apparent that clinker composition and the physical as well as the chemical nature of the hydration products affect setting. Quick setting is thought to be due to the very rapid hydration of tricalcium aluminate and the formation of a sufficient quantity of tricalcium aluminate hydrate to cause setting. Alternatively the coagulation of aluminates and silicates or their hydration products has been suggested as the cause of quick setting. Slow setting on the other hand, although just as obscure in mechanism, has been considered to be due to the presence of tetracalcium aluminoferrite (high Fe_2O_3:Al_2O_3 ratio in clinker) which hydrates to produce colloidal coatings, or to the production of protective coatings of tetracalcium aluminate hydrate on clinker particles when tricalcium aluminate hydrates in the presence of dissolved lime. The presence of sulfate in the clinker and lack of alkalies may also affect the setting times of clinkers.

Addition of gypsum changes the behavior of clinker so that quick-setting clinkers are retarded while slow-setting clinkers are sometimes accelerated. The action of gypsum may go beyond its effects on the setting reactions; it also appears to influence the development of early strength. It is considered that gypsum in the presence of hydrated lime acts as a set regulator retarding rapid setting by modifying the aluminate hydration products, forming calcium sulfoaluminate while it minimizes the formation of colloidal ferrite coatings which occur in slow-setting clinkers. It is not intended to pursue this discussion further here since it is the subject of another detailed paper. However it is clear that there are further reactions and possibilities which cannot be discussed here but which could affect the behavior of cement. The mechanisms of the reactions that occur in the first few minutes of hydration, the nature of the products formed and their function in relation to later reactions warrant much more detailed future study.

It can be seen now that the addition to cement of an accelerating or retarding admixture introduces further complication into a system that is already complex and very incompletely understood. The admixture reactions may be merely additional or counter to those occurring in cement or they may be of a completely different type. Much of the experimental work has been done with accelerators consisting of calcium chloride, sodium carbonate, or other inorganic salts and with retarders consisting of carbohydrates or other organic compounds and such inorganic compounds as phosphates and zinc oxide. The mechanisms of the actions of these compounds are not clearly understood but the overall effects induced in concrete and in oil well cements and grouts under specific environmental conditions are reasonably well known.

Calcium chloride is the most commonly used accelerating admixture. When added in small amounts, usually 2 percent, by weight of cement but sometimes in greater amounts up to 4 percent, it achieves the desired effects of accelerating set and strength development without seriously diminishing the ultimate strength attained. Small additions of sodium carbonate on the other hand accelerate setting but usually reduce the ultimate strength developed. Although the actions induced by these compounds are still largely unknown it is considered that they act in different ways. Calcium chloride acts as a retarder of flash set in clinker in much the same way as gypsum does, presumably due to the formation of calcium chloroaluminate. Its accelerating action in cement appears to be due (1) to the acceleration of the sulfoaluminate reaction between gypsum and tricalcium aluminate, and (2) to a depression of the *p*H, which accelerates the rate of hydration of the silicates. Sodium carbonate on the other hand reduces the calcium-ion concentration immediately, and under these circumstances the retarding action of gypsum is not operative while the

the quick setting of tricalcium aluminate hydrate becomes the major action. Further work is needed to elucidate these setting reactions.

Retardation of setting and strength development in excess of that provided by the usual gypsum addition may be achieved by the addition of various organic compounds. Carbohydrates such as sugars, starches, and cellulose products are most commonly used, while certain acids, particularly hydroxy-carboxylic acids and dicarboxylic acids, gums, albumen, and certain inorganic compounds, such as phosphates and borates, also have marked retarding actions. The action of the organic materials in retarding setting is not clearly understood. It is thought that some retard by adsorption through their hydroxyl groups while others act through their carboxyl groups. This explanation however is probably far too simplified since it does not indicate the mechanism of retardation. A limited amount of evidence has indicated that, after an initial delay, cement hydration proceeds at an approximately normal rate in the presence of sucrose. The development of strength is also delayed for various times which depend directly on the amount of added sucrose. This evidence suggests that initially the additive reacts rapidly with the cement and temporarily retards the rate of hydration. The additive may also affect the nature of the hydration products and the mechanism of strength development.

In the presence of inorganic salts, such as a soluble phosphate, at atmospheric temperature strength development is markedly retarded, but under steam-curing conditions, development of strength occurs readily. Although the cause of this retardation is not understood, it seems that the retarder could affect both the rate of hydration and the strength-developing properties of the hydrated products. Other inorganic salts, such as those of lead and zinc, are retarders. In these instances it is thought that they precipitate as gelatinous hydroxide or as hydrated oxide coatings on clinker surfaces and act as barriers which reduce the rate of hydration. There are sufficient anomalies in the field of accelerating and retarding admixtures to warrant caution in interpreting the available results. Future work should be directed towards determining, as a first step, whether it is the hydration rate or the nature of the hydration product that modifies behavior. Ultimately this work should be directed at understanding the basic mechanisms of acceleration and retardation.

Workability Aids in Freshly Mixed Concrete

It has long been recognized that workability is a property of a concrete mix that permits easy and homogeneous mixing, satisfactory handling and compaction, and suitable surface finishing. Equipment, such as mixers, buckets, buggies, pumps, vibrators, and surfacing screeds and trowels, has been designed to meet the needs of the concrete mixes used and the operations that must be performed. Modification in workability allows a wider choice of materials and mixes, improvement in concrete quality, and economies in power and time consumed in placing and finishing operations. For these reasons, and especially where cement economy is necessary, it is desirable to examine the effects and actions of workability admixtures in relation to costs and economies as well as cementing efficiency and concrete quality. It is these two latter effects that will be examined in greater detail here.

Workability aids may be classified according to their effects on cement paste as (1) dispersers, (2) flocculators, or (3) viscosity increasers.

Although workability depends on a vast number of factors that are capable of simultaneous variation, it will be seen that the most critical factors concern the properties of the paste fraction and the proportion of paste in the concrete mix. Other material factors, such as aggregate gradings, size fractions, and particle shape, also affect concrete workability, while such factors as temperature, cement properties, and standing time may also contribute additional complicating effects. However in this discussion all these factors will be mentioned only briefly since their effects on the two major factors will be largely self-evident.

In a fairly normal 1:2:4 concrete mix, made with reasonably graded sand and crushed stone or gravel of good particle shape and made with a water/cement ratio of about 0.6–0.7 by weight, the paste (cement+water) occupies about 28–30 percent by volume of the concrete. A change in the water/cement ratio alters the paste/aggregate ratio just as surely as a change in the total aggregate or cement. In lean mixes used for mass concrete the paste may occupy as little as 20 percent or sometimes less of the total volume of concrete. As the amount of aggregate is increased (or cement is decreased) the proportion of paste in the concrete becomes limiting in respect to workability, and the concrete becomes harsh and stony. It can be seen therefore that, for a mass of concrete to deform readily or for movement to occur between constituent particles within the mass, there must be some space in which particles can move in relation to each other or rotate without undue interference or interlocking. To allow this movement the concrete mix must contain a sufficient quantity of paste. Adding extra water to a concrete mix is the time-honored but least desirable way of increasing workability because such a practice does not fully achieve its purpose and it introduces a multitude of undesirable characteristics. These may be listed briefly as lowered early and ultimate strengths, increased segregation and bleeding and lack of cohesiveness, increased delay in finishing, increased drying shrinkage, reduced density within the mass, and greater permeability.

Reduction in water/cement ratio therefore appears to be a more logical way to achieve many of the desirable properties of concrete, but the problem of workability must be overcome. If workability is reduced to an extent that the cement paste becomes stiff and the concrete lacks cohesion and cannot be handled and compacted with the available equipment, the theoretical advantages of the lower water/cement ratio cannot be attained. The change in concrete workability as the water/cement ratio is decreased depends largely on the change in physical properties of the paste. Admixtures of various types affect the properties of the cement paste and in this way influence the workability of a concrete mix.

Under normal conditions cement particles in pastes and suspensions tend to be flocculated to some extent. On standing, the flocs sediment, and if the paste or suspension contains more water than can be accommodated within the sedimented bed, segregation occurs so that finally a layer of clear water stands above the bed of solids. Depending on its water content the paste will support aggregate particles of different sizes and density without undergoing deformation and allowing segregation of aggregate. At relatively high water contents pastes tend to be thixotropic, while at lower water contents they tend to exhibit dilatant tendencies. Any reactions that increase interparticle forces, such as premature stiffening or false set, tend to accentuate the dilatant properties of cement pastes. Dilatancy is probably the greatest difficulty to overcome in handling paste or concrete of low water/cement ratio. Unidirectional applied forces are not effective for moving and compacting concrete; vibration is generally much more effective, although excessive amounts may cause segregation.

Admixture materials, such as calcium lignosulfonate, calcium chloride, and many organic materials, which disperse cement particles, reduce viscosity or stiffness compared with that of a flocculated paste. There is a tendency for the finer cement particles to settle slowly in dispersed pastes but ultimately segregation into two layers, a bed of solids and a supernatant layer of water, occurs. On account of the dispersed solid particles settling as individuals, the packing in the bed is often denser than that of flocculated particles and consequently they tend to develop higher strengths. Segregation and bleeding however are much more likely to occur with dispersed particles, and with some dispersing admixtures, notably the carbohydrates, set retardation may be marked.

In concrete some of the defects, such as segregation and bleeding, may be lessened to some extent by reducing the mix water content which at the same time confers the advantages of improved strength and reduced permeability in the hardened paste due to its theoretically smaller capillaries. The workability of the concrete however is being reduced in two ways, (a) by a reduction in the volume of paste, and (b) by an increase in paste dilatancy. Concrete mixes containing dispersing admixtures are not particularly cohesive. Reproportioning the mix by increasing the cement factor may be neither economical nor desirable, since it increases the amount of paste that is capable of undergoing drying shrinkage, it does not entirely overcome the dilatant effects at low water contents, and it may accentuate the segregation problems at high water contents.

The action of dispersing admixtures appears to be due to the adsorption of charged ions onto the surfaces of cement particles which become mutually repulsive. It is possible that other effects may be induced by certain agents or additives that are adsorbed, and even though dispersion may occur it is sometimes masked by a more dominant action. For example, some air-entraining agents may also have a dispersing action, but the effects produced by entrained air exert the major effect on the properties of the paste or concrete mix.

Dispersing admixtures should be used with caution under carefully controlled conditions and for specific purposes where high-strength concrete is required and adequate means of handling and compaction are available. It is not a technique that can be adopted generally without introducing a number of additional problems.

Two new fields in workability improvement may also be discussed. These are concerned with admixtures that (1) increase the flocculation of cement paste, and (2) increase the viscosity of the paste by increasing the viscosity of the water phase.

In contrast with dispersion, enhanced flocculation of cement particles in pastes produces a different set of properties which change the behavior of concrete. Bruere and McGowan [5] have shown that increased flocculation of cement paste can be induced by the addition of various synthetic polyelectrolytes in small amounts which do not exceed 0.15 percent by weight of the cement. These admixtures consisted of various polymers such as polyacrylonitrile and polymethacrylic acid, and copolymers of vinyl acetate-maleic anhydride and isobutylene-maleic anhydride. These copolymers appear to be most effective in increasing the degree of flocculation of cement paste. Although the mechanism of their action is not fully understood, it is thought that these compounds, which have highly charged groups in their chains, are adsorbed on cement particles linking them together. The net result is equivalent to an increase in interparticle attraction which greatly increases the tendency of the paste to behave as one large floc.

The properties of cement paste and concrete which contain the vinyl acetate-maleic anhydride copolymer are of considerable interest and will be described here. Flow of paste containing this admixture, when measured on a standard flow table, was much reduced compared with that of a normal paste at the same water/cement ratio. As the quantity of the admixture increased the flow decreased. In addition, sedimentation volumes were increased as would be expected for strongly flocculated pastes. Pastes consisting of finely ground silica together with additions of this agent and a small amount of calcium hydroxide (0.2 percent by weight of silica) showed similar increased sedimentation volumes. Measurements of the bleeding rates and bleeding capacities of cement pastes made with water/cement ratios varying from 0.5–0.8 showed that the admixture additions increased the former and decreased the latter. Moreover the additions prevented the formation of bleeding channels through these pastes. Similar effects were observed in mortars, and in addition their increased cohesiveness was quite apparent. The action of the admixture on cement paste was maintained in concrete and clearly modified the properties of freshly mixed concrete. In rich mixes the admixture decreased slump and increased cohesiveness, while in lean, mortar-deficient mixes, although the slump was unaffected (zero in all mixes), the cohesiveness was markedly increased even though the water/cement ratio was as high as 0.79. Observation of bleeding and segregation tendencies in two series of concretes that were (a) rodded and (b) vibrated showed that all the control specimens tended to segregate and bleed copiously and to develop bleeding channels and surface craters. Addition of 0.1 percent of the agent to the concrete, however, reduced the bleeding capacity by up to 50 percent, and eliminated bleeding channels, surface craters, and segregation. Compressive-strength determinations indicated that the agent caused only minor changes; an increase for rich mixes and a decrease for lean mixes. The significance of these effects is questionable, and further test results would be desirable to evaluate them fully with respect to cement batch, aggregate types and gradings, mix proportions, compaction method, etc.

The vinyl acetate-maleic anhydride copolymer and other polyelectrolytes used as concrete admixtures possess a number of useful applications. Relatively high water/cement ratios may be used without the undesirable segregation and bleeding effects becoming serious. These are considerable advantages when back-filling inverts or when placing concrete in heavily reinforced sections. Such admixtures can also be used to overcome defects in fine aggregate gradings or particle shape and to reduce the segregation tendencies caused by overvibration. On account of the improvement it effects in workability and in the cohesiveness of lean mixes it could be useful in mass concrete especially as it reduces bleeding and the need for excessive surface cleanup between successive lifts. In transport of concrete, vinyl acetate-maleic anhydride copolymer as an admixture may prove most useful. While the concrete is being mixed or agitated it is readily deformable and workable. When mechanical work is stopped the concrete tends to "freeze" immediately. On this account cement paste or concrete containing this admixture may be regarded as thixotropic rather than dilatant. For this reason it should improve the behavior of concrete that is pumped over long distances as well as of that which is transported in buckets or buggies over long distances. Finally, the green strength of mixes containing the admixture are such that forms may be stripped as soon as placing has been completed and the products may be handled immediately. This advantage of early stripping could be most useful for slip-formed concrete, especially for arches in *in situ* concrete-lined, water-supply pipes.

From the foregoing it would appear that flocculating admixtures would be most useful in improving concrete properties. It should be noted that an admixture such as vinyl acetate-maleic anhydride copolymer does not entrain air and has only a very slight retarding action on setting. It is expected that, compared with normal concrete at equal water/cement ratios, permeability would be either unaffected or probably improved by additions of the agent and that drying shrinkage would not be changed significantly. Flocculating agents such as this admixture possess the useful advantage that they could be used generally and safely without excessive supervision.

Another class of admixture materials, notably those that increase the viscosity of the water phase of cement paste, may find uses in grouts or concrete produced for specific purposes. Compounds such as gum arabic, which increases the degree of flocculation of cement paste very slightly, and methyl cellulose which decreases the degree of flocculation slightly, tend to cause thickening, which is thought to be due to an increase in the viscosity of the water phase. Very little is known about the effects of these compounds on cement paste or concrete setting and strength-gain characteristics. It is considered that they could reduce the rate of segregation and water separation. For these reasons compounds of this type could be worthy of further investigation.

Air Entrainment

During the last 20 yr a tremendous field of work has grown up around the subject of deliberate air-entrainment in concrete. Addition of very small amounts of various surface-active agents to concrete during mixing causes the formation of large numbers of small air bubbles which are entrained in the paste. The presence of these air bubbles as well as the agent modifies the properties of both the freshly mixed concrete and the hardened concrete. The major advantages claimed for entrained air in concrete are improvement in concrete workability and a very considerable increase in durability, especially under adverse freeze-thaw exposure conditions. The importance of this technique warrants a detailed examination of the mechanism of air-entrainment and discussion of the effects produced.

Various types of surface-active agents, which are all long-chain carbon compounds, have been classified by Bruere [6] according to their chemical structures and assessed as air-entraining agents. The agents studied were as follows:

1. Anionic agents such as sodium dodecyl-,

tetradecyl-, and hexadecyl-sulfates and sodium abietate.

2. Cationic agents such as tetradecyl- and hexadecyl-trimethylammonium bromides, decyl- and dodecyl-amine hydrochlorides.

3. Nonionic agents such as polyalkylene ether alcohol and certain long-chain ether-linkage compounds.

4. Miscellaneous agents such as saponin, terpineol, octyl alcohol, and gelatin.

The anionic and cationic agents are all long-chain carbon compounds, which possess terminal active end groups and which are capable of ionizing in solution. The charge on the anionic agents is negative, while that on the cationic agents is positive. On account of their length these molecules display marked dipole characteristics, and at air-water, air-solid, and water-solid interfaces tend to orient in such a way that the hydrophilic end group is attached to the solid or remains in the water while the hydrophobic carbon chain tends to be unwetted and is oriented towards air. When adsorbed on solids these agents change the nature of the surfaces and may convert a hydrophilic or wettable solid surface into a hydrophobic or nonwettable solid surface. On this account these compounds are closely akin to waterproofers, but since the admixture quantities used are small and their solubilities, although small, are significant their waterproofing action is generally not permanent nor completely effective against water movement under a pressure head.

The available information about nonionic agents is very limited, owing in part to the fact that they are complex mixtures of condensates which are difficult to separate. The molecules consist generally of a chain of at least 10–12 carbon atoms comprising the hydrophobic portion together with a hydrophilic portion which contains 5 or more carbon atoms and a terminal hydroxyl group. Very considerable diversity of molecular weight and type (e.g., straight or branched chains) is possible. Although these agents possess polar characteristics, and orient at air-water surfaces, they are not chemically adsorbed on solid surfaces. Saponin and gelatin have good foam capacities and stabilities and appear to increase the surface viscosity of water. Terpineol and octyl alcohol are effective frothers in water since they are capable of causing rapid decreases in surface tension. Their foam stabilities and capacities in water and solutions however are extremely low.

Bruere [6,7,8] has described the effects produced by various surface-active agents when added to cement pastes and mortar. This work has led to a better understanding of the mechanism of air-entrainment in pastes and mortar and in fact forms the basis on which it should be possible to develop new techniques that are of practical significance for concrete.

There are three separate opinions concerning the mechanism by which surface-active agent admixtures alter the properties of fresh cement paste. These give emphasis (a) to the entrained air bubbles, (b) to the surface-active agent, and (c) to contributions by both entrained air and surface-active agent. The first theory, (a), postulates that the entrained air increases the volume and viscosity of the cement paste, and on this account concrete workability and cohesiveness are improved and segregation and bleeding are reduced. Since the entrained air bubbles are generally small and consequently possess a large total surface area, they are thought to behave somewhat like fine mineral admixtures. Their ability to deform under applied forces assists their lubricating action while their low density and consequent buoyancy is thought to assist in counteracting the settlement of solid particles.

The second theory, (b), suggests that the surface-active agent itself has the major influence in altering the properties of cement paste and that the entrained air has only a minor effect on such modified properties as workability, cohesiveness, and reduced segregation and bleeding. The surface-active agent is assumed to be adsorbed on cement-particle surfaces forming oriented hydrophobic films which act as boundary lubricants. In this way workability is thought to be increased. As a result of adsorption of surface-active agent on cement particles, the degree of flocculation of the paste is increased, and this increase is thought to be the reason for the observed reductions in segregation and bleeding in concrete.

Much of the evidence supporting these two different theories is indirect and was obtained by studying systems that contained both surface-active agent and entrained air. Hence the third theory, (c), which postulates that both the surface-active agent and entrained air contribute to the altered properties of cement paste and concrete, requires that the effects produced by the agent be studied separately from the compounded effects of agent and entrained air. Such a study could only be made when a technique had been developed for mixing cement paste reproducibly in the presence of surface-active agents without air bubbles being entrained. This method, which has been described by Bruere [7], has been used successfully and consists essentially of mixing cement paste in a virtually sealed vessel that is always completely filled, so that a vortex cannot form around the stirrer and air cannot be stirred into the paste. After a preliminary mixing the required amount of surface-active agent is injected into the paste and mixing is completed.

The viscosities of cement pastes, containing different surface-active agents added in a range of concentrations and without the complicating effect of entrained air, show some interesting variations. Anionic agents increase the paste viscosities significantly at low agent concentrations (0.01 percent by weight of cement). The agents are adsorbed on the cement particles, which tend to become hydrophobic, and on account of their increased interparticle attraction, flocculated to an increased extent. Flotation tests clearly confirm the adsorption of anionic agents on cement particles.

Cationic agents (e.g., hexadecyl-trimethyl ammonium bromide) also increased paste viscosity when used in low concentrations (below 0.05 percent by weight of cement). Under these contions the agent is adsorbed on the cement particles in such a way that the nonpolar ends of the molecules are oriented towards the water, the surfaces tend to become hydrophobic, the degree of flocculation increases, and the paste becomes more viscous. At higher concentrations of agent however a second layer of surface active molecules is adsorbed with the nonpolar ends oriented towards the particles and the polar ends oriented toward the water. Since the polar ends are hydrophilic there is a reversal in behavior and the paste becomes less viscous. It will be noted that with anionic agents cement paste does not show this reversal in behavior because the concentrations of the agents in solution are always low on account of their precipitation as sparingly soluble calcium salts.

Nonionic agents have virtually no effect on the viscosity of cement paste, while admixtures such as calcium lignosulfonate and saponin decreased paste viscosities at all concentrations. Both calcium lignosulfonate and saponin reduced interparticle attraction, the former by a dispersion mechanism and the latter by a protective colloid mechanism.

In the presence of entrained air and over a range of water/cement ratios the viscosities of pastes containing an anionic agent increased rapidly, whereas the viscosities of pastes containing saponin studied under the same conditions increased very slowly as the quantities of entrained air increased. Since it has been shown that air bubbles entrained in pastes containing saponin are not attached to cement particles, the increased viscosities in this instance must be due to the increase in surface area which follows from the fact that entrained air bubbles act as fine, weightless solid particles. The increase in paste viscosity due to entrained air only just exceeds the decrease in viscosity due to the action of saponin in reducing interparticle attraction. The increases in paste viscosities, which are produced by anionic agents in the presence of entrained air, exceed the sum of the effects caused separately by the interparticle attraction and the increased surface area due to air bubbles. Consequently at least one other factor must be operative. It is considered that these increases could be due, at equal air contents, to a smaller mean bubble size or to bubbles adhering to cement particles acting as bonds, which increase the aggregation of particles and form a large cohesive floc.

Examination of data showing the bleeding rates and capacities of pastes containing various surface-active agent additions with and without entrained air confirms the foregoing conclusions. In general the bleeding rates and capacities of cement pastes of limited water contents are reduced by amounts which depend on the degree of flocculation and the quantity of entrained air and the interaction of these two factors.

In connection with the mechanism of air-entrainment in cement pastes a considerable amount of data has been accumulated on the foam stability and foam capacity of various surface-active agents in contact with cement and their reactions with cement and silica particles. From all this data two major factors have emerged as necessities for air entrainment to occur. The surface-active agent must (1) possess some foam stability and foam capacity tendencies after coming into contact with cement particles and undergoing adsorption or chemical reaction, and (2) the surface-active agent should be adsorbed on the solid particles to render their surfaces hydrophobic so that air bubbles adhere to them. The significance of this latter factor can be readily demonstrated by the action of flotation activators and depressors on air-entrainment in silica pastes. An agent such as sodium dodecyl sulfate, which does not float silica and will not entrain air in a silica paste, can be made to do both by the addition of calcium hydroxide. The reverse behavior can be achieved with dodecylamine hydrochloride, which floats silica and entrains air in silica pastes, by the addition of gelatin. With anionic agents, such as sodium dodecyl sulfate in cement paste, the calcium salt, which is precipitated, appears to be capable of stabilizing bubbles and of sufficient solubility to produce the necessary foaming capacity in the solution.

Entrained air bubbles that are adsorbed on solid surfaces are very stable and cannot be readily removed. In hardened cement pastes cured under normal conditions, the bubble replicas retain their spherical shape. It is most likely that the adsorbed cement particles form a relatively undeformable coating on the bubble surfaces.

Saponin behavior in pastes according to the foregoing mechanism is anomalous because the entrained air bubbles are not attached to the solid surfaces. However saponin possesses a high foam capacity and forms fine bubbles which do not coalesce or escape readily, probably on account of the anomalous properties (e.g., viscosity) of thin films consisting of saponin-water mixtures.

A few brief comments may now be made on the effects of entrained air in concrete. Improvement in concrete workability is abundantly apparent on account of the modification of paste properties. The major defect of entrained air is its tendency to reduce strength, and this effect may be minimized by minor adjustments in mixing water and sand content. The major advantages in hardened concrete are decreased permeability and greatly increased resistance to frost action. These two advantages are probably interconnected. The mechanism by which frost action damages concrete is still incompletely understood. However two theories based on observation and experiment have been proposed and these suggest that damage is due to (a) development of hydrostatic pressure as a result of water freezing within limited spaces in the cement gel or (b) the formation of ice in zones where, by an increase in volume, mechanical disruption occurs. The former theory would apply to the more rapid rates of freezing whereas the latter would apply to slower rates of freezing and presupposes the presence of zones where ice can form. Frost damage can be alleviated by providing adequate spaces distributed throughout the concrete to accommodate the volume increase produced by the water-ice phase change. Entrained air bubbles distributed uniformly throughout the paste and spaced no farther apart than a minimum spacing distance (Powers [9]) are considered to be space into which water can move, and ice can form without building up disruptive pressures within the paste. There is now ample field evidence to show that air-entrained concrete possesses durability under adverse exposure conditions which far exceeds that of non-air-entrained concrete.

Future work on air-entrainment may well be developed along the lines of applying the theory of air-entrainment to solving problems that are concerned with concrete construction and durability. One line of work which suggests itself is contained in the work of Bruere [6] and concerns the uses of mixed surface-active agents which taken singly may be inefficient but taken together, so that their specific effects are additive, may be very efficient. An example of this type of action would be the use of a surface conditioner such as hexadecyl trimethyl ammonium bromide, and a foaming agent such as terpineol or octyl alcohol. If, by a judicious choice of admixture amounts of suitable agents, fine, stable air bubbles can be entrained in amounts that are constant and insensitive to agent concentration, and mixing vigor and time, the need for constant and rigorous control could be minimized without impairing concrete quality. Further, if bubbles that are sufficiently fine and uniformly distributed can be entrained in concrete, the total quantity of entrained air could be minimized. Such an advance would minimize strength losses and variations in concrete but at the same time permit the retention of the desirable properties such as permeability reduction and frost resistance.

Waterproofers and Permeability Reducers

Waterproofness, or the ability of concrete to resist the movement of water through it, is an important characteristic that is affected by two major factors, namely (1) the quality and condition of the concrete, and (2) the method by which water is made to penetrate it. In general it is found that compacted cement pastes made with a water/cement ratio no greater than about 0.27 and high-quality, fully compacted, and properly cured concrete are virtually impermeable to liquid. However in concretes there may be honeycomb areas, shrinkage cracks caused by drying, joints, poorly bonded areas under reinforcement, or large aggregate particles, and all of these constitute positions or flaws through which water under pressure may move readily. Consequently, procedures or admixtures that assist the production of dense, well-compacted, well-cured, and volumetrically stable concrete reduce permeability and increase waterproofness. Some such admixtures are not necessarily waterproofers. For example calcium chloride admixture may assist in reducing concrete permeability by improving workability and compaction, and by reducing damage that may result from inadequate curing. It is not a waterproofer in the true sense of the term. Air-entraining agents, although surface adsorbed on cement particles, are not necessarily good waterproofers either, even though they may assist in reducing concrete permeability. Their waterproofing action due to their conditioning surfaces is generally transitory on account of the small quantities used in concrete, their slight solubilities, and the tendency for large quantities of calcium hydroxide to be dissolved under moist conditions, and redeposited under drying conditions to mask or modify the conditioned surfaces. For many applications cement itself may be regarded as the best admixture, for an increased cement factor (richer mix) will often give adequately waterproof concrete.

Water penetration of concrete may occur under the action of a head of pressure or as a result of capillary forces. Under the action of pressure, water penetration usually takes place from one external surface while movement under the influence of capillary forces may occur in all directions. The quality of the concrete, and especially the density of the paste, affects both the rate and distance of penetration. The relationship between capillary movement and evaporation under suitable atmospheric conditions is an interesting one since it may induce the development of efflorescence on external surfaces in positions where the rate of evaporation equals the rate of water movement.

A number of different types of admixtures may be used to restrict water penetration and movement through concrete. These materials, which have different waterproofing actions, may be used as integral admixtures or as surface treatments on hardened concrete. Both types of treatment are useful; the former acts throughout the concrete mass while the latter forms only a surface film or skin which retains its effectiveness only as long as it remains undamaged. It may be noted here in passing that membrane curing compounds may be regarded as surface waterproofers which act in reverse, and constitute a useful technique for curing under difficult field conditions. Waterproofed concrete also demands that curing be continuous and commenced early because if it dries out it is virtually impossible to rewet it.

Integral waterproofing admixtures are of two major types; namely (a) water repellents (e.g., soaps), that may react with cement and tend to condition the surfaces of the solids, and (b) inert hydrophobic liquids such as mineral oils or asphaltic emulsions. The usual water-repellent-type admixtures generally consist of compounds such as calcium or ammonium stearates or oleates. The calcium compounds are practically insoluble in water but can be mixed with concrete. Care must be taken to insure that they are uniformly distributed throughout the mix. The ammonium compounds react very readily with cement and precipitate the calcium compounds. Both are added usually in small quantities (0.2 percent by weight of cement) because in large quantities they tend to cause severe frothing and to lower concrete strength. Butyl stearate, which is liquid at usual summer temperatures, does not usually cause such severe frothing as the other stearates and may be used in greater admixture quantities with less risk of serious strength reduction. It appears that butyl stearate is hydrolyzed slowly so that during the mixing period only a minor portion of the admixture quantity can react with cement; the remainder acts initially as an inert admixture liquid but slowly hydrolyzes and reacts with cement. Heavy mineral oils when used as waterproofing admixtures do not seriously reduce strength and appear to act as stoppers in capillaries. Asphaltic emulsions, which cause greater concrete strength losses than mineral oils, appear to act in much the same way when the concrete is allowed to dry sufficiently to permit the emulsion to break.

Although integral waterproofers have proved useful under some circumstances, especially in minimizing capillary movement, they have not always prevented water penetration and movement under applied pressures. The permeabilities of hydrated cement paste and concrete are not always completely overcome, and some reassessment of what is occurring is needed. The positioning of water repellents in the hydrated paste may not be particularly satisfactory since, as hydration proceeds, there is an enormous increase in new surfaces that may be completely unaffected by the admixture. Moreover as concrete undergoes cracking it is probable that the new crack surfaces are incompletely conditioned by the waterproofer. The inert admixtures would not be expected to be distributed more efficiently by the hydration process or to stop effectively any cracks that develop after the concrete has hardened.

A number of new types of material have been studied. Silicone compounds have some uses as water repellents but are unsatisfactory when used as waterproofers. Some types of rubber admixtures however appear to have possible uses as waterproofers.

On account of cost or to make the best use of their properties some film-forming materials may be used as surface coatings on hardened concrete to prevent water penetration. Various compounds have been used in this way, and some are known to penetrate into the concrete for considerable depths. Mineral or vegetable oils, waxes dissolved in solvents, bitumen emulsion or paint, and plastics have been used successfully to produce coherent films, which act as water barriers or strongly hydrophobic surface zones, while water repellents such as soaps and silicones have not proved successful as surface treatments. All surface coatings however suffer the defects of being exposed to weathering action, deterioration of bond with the concrete, nonuniform thickness, a tendency to rupture as a result of volume instability of the concrete or as a result of mechanical damage. Future work should be aimed at improving the action of water-proofers used integrally or as surface treatments. Such compounds could greatly assist in reducing attack by aggressive solutions and may simultaneously lead to improvements in such properties as concrete strength or abrasion resistance of surfaces.

Corrosion Inhibitors

Concern has been expressed at the corrosion of reinforcement steel in concrete subjected to certain environmental conditions. In recent times attempts have been made to prevent serious corrosion even under very adverse conditions of production, curing, and exposure by the use of admixture materials. The studies that have been made in this field seem particularly pertinent to the present discussion of admixture materials. In recent papers Shalon and Raphael [10] and Bäumel [11] discussed the action of dissolved salts as well as a number of other variables on reinforcement corrosion.

Under normal exposure conditions, steel reinforcement, covered by more than an inch of dense concrete which forms a continuous adherent coating on the steel surface, undergoes little or no corrosion due to chemical attack. The high alkalinity of the cement solution, which generally exceeds *p*H 12, produces a passive oxide layer on the steel and inhibits further corrosion. Carbonation of the hydrated cement proceeds at a very slow rate which diminishes further as the surface undergoes carbonation. In addition dense concrete is relatively impermeable to water. Incompletely compacted concrete or lean concrete is permeable to gases and water and does not afford satisfactory protection, and corrosion eventually occurs. Salts or compounds which reduce the solution *p*H to less than 12 promote corrosion, and in the presence of certain strongly ionized soluble salts an electrolytic cell action may occur and cause severe steel corrosion. Other corrosion mechanisms, such as the action of stray electric currents, are not of great interest here because they are due to installation leakages rather than to chemical action.

The practice of adding an accelerator, such as calcium chloride, to concrete tends to accentuate the risk of steel corrosion. Since it is a fairly general practice in concrete-products manufacture to steam cure with atmospheric-pressure steam, in order to accelerate strength development so that the forms can be stripped at early ages, the addition of calcium chloride as a set accelerator leads to marked corrosion of reinforcing steel. Steam curing appears to activate the corrosion reactions in the presence of calcium chloride and to accelerate their rates. Measurements of tensile strength can be made on mortar specimens in which the load is applied to two steel pins which are merely butted together in the center of the specimen. Under moist or wet curing conditions, even with calcium chloride admixture in the mortar, the tensile strengths are satisfactory after exposure for 1 yr. Steam-cured mortars however show very marked tensile-strength reduction when tested at 7 and 28 days depending on the amount of admixture added. These mortars, in contrast with those of high tensile strength, show numerous surface cracks filled with brown iron oxide; the steel pins are always severely corroded while those embedded in mortars cured under moist or wet conditions are relatively bright and uncorroded.

On account of the technological importance of accelerating setting and strength development by accelerator additions and steam-curing it is necessary to use a corrosion inhibitor which preferably also has the accelerating action of calcium chloride. Experiments in these laboratories have indicated that stannous chloride possesses all these desirable properties and can be substituted for calcium chloride as an accelerator that does not cause steel corrosion even under steam-curing conditions. Other salts such as cuprous chloride, chromous chloride, and cobaltous chloride possess similar but less marked acceleration and corrosion-inhibition properties. It appears necessary to use salts in the reduced condition and to ensure that the mortars are dense, otherwise their useful effects are nullified and corrosion occurs. The corrosion inhibition is thought to be due to the metallic ion tin, copper, chromium, etc. acting as a reducing agent and possibly plating the steel and protecting it from further chemical action.

There are also numerous possible combinations of corrosion inhibitors that can be used in conjunction with a setting and strength-development accelerator. In this instance calcium chloride could still be added as an accelerator while the corrosion inhibitor would be added to prevent reinforcement corrosion. These possibilities would seem to indicate a fruitful field for future work. The major criterion of successful action is an inhibitor which will prevent the corrosion of steel by calcium chloride under steam-curing conditions. If specimens are stored in a water-vapor saturated atmosphere after steaming, the optimum conditions for corrosion failure exist and a short testing period will be attained. Under these conditions control specimens containing calcium chloride are generally severely cracked within 10 days of steam-curing. Careful testing of corrosion inhibitors would be essential to ensure that they do not adversely affect the reinforcement-concrete bond or have other adverse effects on concrete. This whole subject is still in its early stages of development, and it is expected that a number of new compounds or procedures will be devoloped for controlling reinforcement corrosion.

Other Admixtures Used for Various Purposes

Apart from the admixture materials already discussed there are a number of other admixtures, added materials, or treatments that involve adding material to concrete, all of which have rather restricted uses for some specific purpose or product. Although it is not intended to give an exhaustive account of these admixtures or their uses, some of the more typical materials and techniques will be mentioned.

When quantities of gas, in excess of those that can be obtained by air-entrainment, are required in concrete, for example in lightweight or foamed concrete, it is usual to use a gas-forming agent such as finely divided aluminum powder. Alkali derived from the cement reacts with the aluminum to form hydrogen gas which is evolved as small bubbles which tend to bloat the concrete. Other gas-forming admixtures consist of finely divided metallic zinc and magnesium, or mixtures of hydrogen peroxide and bleaching powder. Care needs to be exercised in the case of all these agents on account of two major difficulties. Their rates of gas evolution are temperature dependent, and it is necessary to synchronize this with cement setting. In addition the gas bubbles, unlike those entrained with some surface-active agents, are unstable with respect to their size and position in cement paste. They tend to coalesce and escape readily. The technique of bloating to a limited extent may be used to counteract the settlement of concrete especially when used for back-filling or placing between vertically fixed points.

As a means of counteracting the drying shrinkage of portland cement much experimental work has been done, particularly in Europe, on expanding cements. Mixtures of sulfoaluminous cement and ground slag in varying proportions may be added to portland cement to give a delayed but controlled expansion. An admixture such as finely divided iron together with an oxidizing agent in the presence of moisture may also produce an expanding cement. The major problems with these materials and admixtures appear to lie in adequate control over the expansion processes and in insuring that internal expansion occurs in positions that adequately counterbalance drying shrinkage.

The use of finely ground limestone or chalk as an admixture in portland cement, sometimes in conjuction with an integral air-entraining agent, to produce masonry cement is fairly common. These cements have been developed to meet the specific requirements, namely a workable, cohesive, and water-retentive mortar for bricklaying.

Admixtures of various types may be used in concrete or other products or in certain parts of structures to improve or obtain desired properties.

Asbestos fiber used in asbestos cement products permits the production of relatively light sheets, pipes, and special shapes that possess suitable strength and flexibility. Recently plastic admixtures, such as polyvinyl acetate, have been used as surface densifiers and hardeners in floors subjected to heavy wear while rubber has been used in attempts to improve resilience. Pigments and artificially prepared colored aggregate may be used to achieve desired artistic and architectural effects.

In concluding this section some comment may also be made on the use of surface treatments on concrete. Although such treatments may not strictly be regarded as admixtures, the fact that in many instances the treatments penetrate for considerable distances into the concrete and modify the surface properties of the concrete very markedly in part at least justifies their inclusion here. Most surface treatments are applied for specific protective purposes. Concrete surfaces have been modified by the use of various materials as paints. Solutions of magnesium and zinc fluosilicate and sodium silicate, oils, bitumen, and mastics have been applied, usually as protective coatings but in the case of the solutions sometimes as surface densifiers and hardeners. There are however two other less well-known treatments that deserve mention. Gaseous silicon tetrafluoride penetrates concrete surfaces and reacts to form calcium fluosilicate which is relatively inert to acid attack. This treatment has been used as a means of protecting concrete in sewers from attack by sulfuric acid formed by bacterial oxidation of hydrogen sulfide gas. The other treatment consists of subjecting concrete to heavy carbonation. Carbon dioxide can be made to penetrate concrete for very considerable distances and may be used as a densifying and stabilizing treatment. In addition it has been observed to have a marked retarding effect on the rate of sulfate attack on treated mortar and concrete when immersed in aggressive solutions. It is expected that such treated concrete would behave satisfactorily if embedded in neutral or alkaline aggressive soils. Both of these gaseous treatments appear to be more effective than the application of appropriate paint treatments in achieving protection of hardened surfaces.

These comments are intended to indicate the broad and ever-increasing scope for the successful use of cement paste, mortar, and concrete. On account of the increasing number of possible uses for concrete there will undoubtedly always be a field for the development of new admixtures that improve specific properties of concrete, assist its production and handling, and permit the development of new products.

The Future

Any attempted assessment of the future developments and improvements that may be achieved by using admixtures must take into consideration the problems that are inherent in the materials, cement and concrete, and in the stages of development reached in the different and often separate fields in which concrete is used. The uses of concrete in different forms of construction, such as mass concrete, thin unreinforced slabs, reinforced and prestressed concrete, are varied while the handling and construction methods adopted, namely ready-mixed concrete, pneumatically applied mortar, tremie and pumped concrete, grouts, and the usual batch-mixed concrete, are similarly variable. Hardened concrete is exposed to extremely variable environmental conditions, such as being buried in soils and immersed in water of all types; it is subjected to a wide range of atmospheric conditions and to mechanical stressing and abrasion. Within limits the same materials are used for making concrete; the conditions, to which these materials and the structures made from them are exposed, are extraordinarily different and variable. The questions that arise here are what defects and problems arising from the materials, structure design, and the interaction between the structure and the environment are important and whether suitable admixture materials can be used or devised to overcome or alleviate these defects and problems.

The major problems encountered in concrete materials are concerned with strength, volume stability, and durability. Although improvements are desirable in many directions, it can be said that in general ways can be found to mix, handle, and place concrete reasonably satisfactorily. Structure design however is handicapped by the three above-mentioned major problems all of which are to a large extent problems that are inherent in hardened cement paste.

The strength of concrete is a complex property which has many different facets. The nature of the forces that produce coherence within the hydrated cement paste, in other words the intrinsic strength of the paste, are largely unknown. The behavior of cement paste or concrete under the influence of applied stresses, which is more generally regarded as its strength, has been studied extensively. These experimental determinations of mechanical strength have indicated clearly that cement paste and concrete are relatively strong in compression but relatively weak in tension. This weakness in tension can be counteracted by designing a composite unit that is adequately reinforced. The presence of steel reinforcement however introduces entirely new problems concerned with bond and stress transfer from concrete to steel. It is clear that unless the reinforced concrete behaves as a single unit its designed advantages will not be attained. Recently it has been shown that by the use of suitable treatments with epoxy resin the steel-concrete bond can be increased by several hundred percent. This increase is such that it has revealed once again the serious tensile weakness that is inherent in portland cement. Consequently new ways of increasing strength greatly in excess of that attainable at present need to be investigated. The use of strength-increasing admixtures and techniques appear to offer some possibilities of success since these may possibly be adapted to modifying the hydrated products and their properties, increasing the paste density, eliminating reactions that cause or contribute to internal stress, volume instability, and cracking, and increasing cement paste-aggregate bond.

The phenomenon of volume instability is another major defect of concrete. It has been noted already that cracking contributes to the low measured concrete strengths. Volume instability may be of two types, that induced by changes within the cement paste as a result of hydration and within the hydrated cement paste as a result of loss of water (drying shrinkage) or other reactions that may induce expansion, and that which is a characteristic of the mass but which occurs in the paste, known as creep or plastic deformation. Of all these volume changes, that caused by drying is probably the most serious because it is least amenable to control. While the presence of large aggregate in concrete undoubtedly minimizes the overall dimensional changes of the mass and restricts the number of major cracks developed as a result of drying shrinkage, it does not prevent the virtually discrete pockets of mortar within the mass from shrinking individually and developing large number of minor cracks. Consequently any technique or admixture that will minimize or prevent drying shrinkage or cracking must contribute enormously to future concrete technology. Increases in the intrinsic strength of hydrated cement may contribute considerably towards increased volume stability, and it is probable that creep, or plastic deformation under the action of applied forces, would be reduced. Further studies of the mechanism of creep are clearly indicated since these could assist in elucidating the weaknesses of hydrated cement paste and suggest methods for their correction.

The characteristic of cement paste and concrete that will receive greater future attention is durability. Much of the earlier discussion in this paper has been concerned with admixtures that, either in themselves or in the way that they assist in the handling of concrete or modification of hardened concrete properties, contribute to improved durability. It would not be amiss to indicate again here that admixture materials, such as more efficient air-entraining agent, workability aids, waterproofers and permeability reducers, reinforcement corrosion inhibitors, and treatments that prevent attack by aggressive solutions, will have a large and important part to play in the future of concrete.

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Discussion

K. R. Lauer

These comments pertain to that portion of the paper dealing with air-entrainment. In general the two major conclusions of Bruere were confirmed by laboratory investigation, namely the surface-active agent must possess some foam stability and foam capacity tendencies after coming into contact with cement particles and undergoing adsorption or chemical reaction; and the surface-active agent should be adsorbed on the solid particles to render their surfaces hydrophobic so that air bubbles adhere to them.

There is also evidence that the mixing procedure used has an important effect on the resulting air-entrainment. For example, the use of a Hobart N–50 mixer at high speed for 5 min readily entrained air with sodium lauryl sulfate in silica pastes. A 0.005M solution entrained 66 percent air in a paste with w/c of 0.60.

A method involving the use of a surface-tension–concentration curve for determining the concentration of an air-entraining agent in the filtrate proved successful. For the method of mixing used (Hobart N–50 at high speed for 5 min) and for representative agents of the anionic, cationic, and nonionic groups there appears to be a straight line relationship between the air content and the filtrate concentration of the mortar (fig. 1).

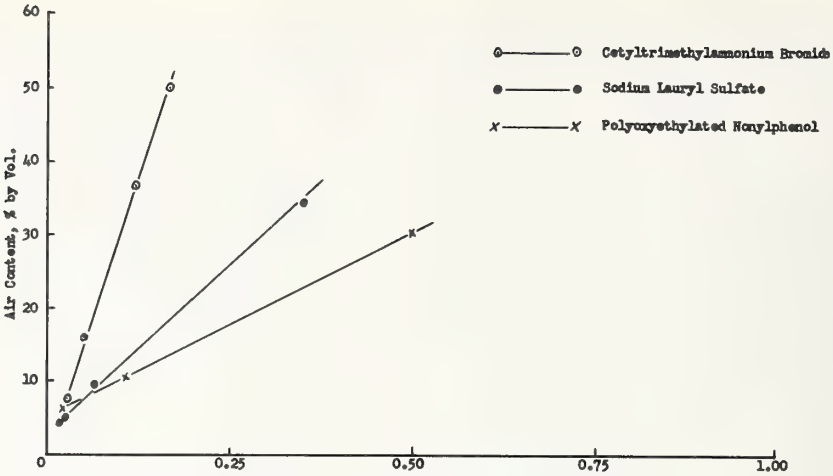

FIGURE 1. *Air content vs. concentration of agents in filtrate.*

Concentration of agent in filtrate, mM.

The differences in mineralogical composition associated with such aggregates as limestone, quartz, and natural sand had little effect on the air entrained in mortars. Angular aggregate increased the air content of mortars compared to those containing rounded aggregate.

Discussion

J. H. Taplin

In his paper, Vivian mentions several types of materials which retard the hydration of portland cement. He suggests that hydroxyl groups are active in some compounds and carboxyl groups in others. Hansen [1][1] suggested HO–C–H as the active group and Steinour [2] generalized this to the simple hydroxyl group in order to include certain inorganic substances. The data presented below indicate that HO–C–C=O is very active. In fact, it appears to be a general rule, that for an organic substance to retard cement, it must have at least two oxygen atoms each bound to a single but different carbon atom in such a way that the oxygen atoms can approach each other.

The data were obtained from paste specimens with a water-cement ratio of 0.30. Unless otherwise stated, the substances were added as one percent by weight of the cement. Soluble substances were dissolved in the mixing water, insoluble solid substances were mixed with the dry cement, and insoluble liquid substances were added simultaneously with, or immediately after, the mixing water. The extent of the hydration was determined after 7, 17, 48, and 170 hr, by a method which involves determining the ignition loss at 540 °C of paste previously dried in an atmosphere of steam at 125° C. This method and the composition of the cement have been described previously [3]. The controls gave hydration values (H/C) close to 0.029, 0.069, 0.104, and 0.114 for the various curing periods. The paste stiffened at an H/C value of about 0.020 and hardened at about 0.050. With some substances (malic, α-ketoglutaric, gluconic, and dihydroxytartaric acids) the paste remained fluid ($H/C<0.010$) for more than a week, but with other substances the paste went stiff more or less rapidly, even though it may have taken several days to harden. If the H/C value at 17, 48, or 170 hr was 0.030 below that of the control then this retardation was considered significant. If the retardation was significant at only one curing period (usually 17 hr) then the substance was classified as a weak retarder. If the retardation was significant at two or three curing periods (which always included the 17-hr value) then the substance was classified as a strong retarder.

Table 1 is a classification of substances as retarders on this basis. Sections (a), (b), and (c) consist of simple compounds based on aliphatic chains of one, two, or three carbon atoms. It will be seen that all the retarding substances contain the group HO–C–C=O except glycerol. Oxalic and lactic acids are exceptional in that they contain the group but do not retard.

Section (d) contains substances based on a chain of four carbon atoms. Those which have the HO-C-C=O group retard. This section also contains retarding substances in which the oxygen atoms are not on adjacent carbons although, from the negligible activity of fumaric (as compared with maleic) acid, it would appear that the oxygen atoms must be able to approach each other.

Sections (e) and (f) contain some additional organic compounds. However caution must be applied in interpreting the results for substances such as quinone and pyrogallol which decompose rapidly in cement paste.

If we assume that organic substances retard by adsorption, then there are two alternative surfaces where this process might be effective:

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Classification of substances in terms of their ability to retard the hydration of cement* [a]

Section	Retarding effect		
	Negligible	Weak	Strong
a	Methanol Sodium formate Formaldehyde (Diethoxy) methane		
b	Ethanol Calcium acetate Acetaldehyde Glycol Glyoxal Oxalic acid Dioxane		Glycol aldehyde Glycollic acid
c	*n*-Propyl alcohol Isopropyl alcohol Propane 1:3 diol Propane 1:2 diol Allyl alcohol Propionaldehyde Acetone Propionic acid Acrylic acid 2-Chloropropionic acid Malonic acid Hydracrylic acid Lactic acid	Glycerol Tartronic acid Butyl lactate Glyceric acid	Acetol Pyruvic acid Glyceraldehyde Dihydroxyacetone Ketomalonic acid
d	Fumaric acid Aldol Succinic anhydride	Maleic acid Erythritol Succinic acid Acetoin	Malic acid Maleic anhydride Tartaric acid Dihydroxytartaric acid Ethyl acetoacetate
e	Chloral hydrate EDTA (disodium salt) Glycine Urea Adipic acid 4-Hydroxypentane-2-one Cupferron	Diacetone alcohol Acetyl acetone Phorone 8-Hydroxyquinoline	α-Ketoglutaric acid β-Ketoglutaric acid Gluconic acid Citric acid 3 percent EDTA (disodium salt) Sucrose Glucose Fructose Sorbitol Pentaerythritol
f	Anthraquinone Phenol	Hydroquinone Salicylaldehyde Phloroglucinol Resorcinol 1:4 Naphthoquinone Chromotropic acid	Quinone Catechol Pyrogallol Gallic acid 1:2 Naphthoquinone Sulfonic acid
g	ZnO (in 3.6N NaOH solution) BeO (in 3.6N NaOH solution) As_2O_3 Sb_2O_5 Pb_3O_4 $CrCl_2$ $K_2Cr_2O_7$ Cu_2O CuO $HgNO_3$ $HgCl_2$ $SnCl_2$ NaH_2PO_2 $K_4P_2O_7$	$PbSO_4$ $Pb(NO_3)_2$ H_3BO_3 Sb_2O_3 CdO V_2O_5 $Cu(NO_3)_2$ $Na_2S_2O_5$ Potassium trithionate Sodium tetrathionate Sodium hexametaphosphate Concentrated ammonia	ZnO $ZnCl_2$ $ZnCO_3$ ZnO (in ammonium hydroxide solution) $BeSO_4$ PbO B_2O_3 As_2O_5 $Na_4V_2O_7$ Metaphosphoric acid Borax

[a] All substances added as 1 percent by weight unless otherwise indicated.

(1) on the surface of the clinker minerals so as to protect them from attack by water, and (2) on the surface of a coherent coating of hydration products so as to prevent the transport of material to or from the clinker surface. The explanation associated with this second adsorption process is similar to that suggested [3] to explain the limited hydration of low water-cement ratio paste. The explanation of this limited hydration phenomenon is that a rate-determining transport process through the hydration products ceases when the water voids become filled with products. (Although we can only speculate on the nature of the chemical species which might be involved in such a transport process, it appears unlikely that it would be water because of the relatively high concentration and mobility of this substance compared with, for example, calcium and silicate ions.)

Section (g) of table 1 contains inorganic substances. Substances such as boric oxide and the salts of the polythionic acids may provide anions which adsorb in the same way as organic retarders. However some inorganic substances such as zinc oxide and beryllium sulfate will not retard if they are added as solutions in alkali. It is not yet known if this is due to the presence of the alkali itself or because these substances can only act through their cations. These cations may exchange with those surface cations upon which the organic substances adsorb and both processes may have the same effect of either (1) stabilizing the clinker surface or (2) blocking the surface diffusion of material through the products.

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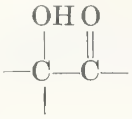
Closure

H. E. Vivian

K. R. Lauer has indicated quite correctly that mixing vigor, which may be equated to speed of stirring, affects entrainment of air in pastes. It should be remembered, however, that both the consistency of the paste and the concentration of air-entraining agent will also affect the volume of air entrained. Bruère worked at rather lower concentrations of air-entraining agents than those used by Lauer. Although air can be entrained in silica pastes in the absence of calcium ions at high *p*H, the entrained air is unstable and on standing the paste readily segregates into separate layers. Undue emphasis should not be placed on the correlation between volume of entrained air and concentration of agent in the filtrate since very considerable difficulties are involved in obtaining reliable concentration data from surface tension measurements on filtrates from complex systems such as cement paste. It is considered that the surface area of sand particles is too small to affect the volume of air entrained in mortar significantly but that angularity in sand particle shape could increase the volume of entrained air by increasing local turbulence during stirring.

J. H. Taplin has noted that organic admixtures containing 2 oxygen atoms bound to adjacent carbon atoms as—



$$-\underset{|}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-$$

generally act, with few exceptions, as retarders. The mechanism of retardation of setting appears in many instances to be caused by adsorption of the retarder on solid surfaces in such a way that the rate of hydration is reduced. It is also possible that some admixtures may change the chemical composition of the hydration products and may modify their strength developing properties.

Since the original paper was written further work has shown that marked changes can be induced in the behavior of hydrating clinker compounds by the use of admixtures. The importance of all these studies cannot be overemphasized since they could lead to a clearer understanding of the chemical reactions and physical changes that occur as cement hydrates.

SESSION VIII. SPECIAL CEMENTS

Paper VIII–1. Stressing Cement and the Mechanism of Self-Stressing Concrete Regulation*

V. V. Mikhailov

Synopsis (By editor)

Soviet waterproof expansion cement, called WEC, was developed in 1942. It is obtained by dry grinding of high alumina cement, gypsum, and artificial hydrocalumite (C_4AH_{13}). Its functioning is based on quick formation of high-sulfate sulfoaluminate (ettringite). It quickly develops high strength, provides full shrinkage compensation, sufficient expansion, and great watertightness. It is excellent for repair and restoration of concrete structures, and as a waterproof layer.

Soviet stressing cement, called SC, is a more recent development, and research on it is continuing. It has three components: finely ground portland cement clinker, high alumina cement, and gypsum. Typical percentages are 66:20:14 when the portland cement has moderately high C_3A content. Use of a low percentage of water (25–30 percent) in 1:1 mortar gives good results under hydrothermic treatment (up to 100 °C) after a day of natural hardening. Low-sulfate sulfoaluminate forms first. Recrystallization to high-sulfate sulfoaluminate in the already hardened mass causes expansion, with retention of the bond to reinforcing steel, thus stressing the latter. High strength, watertightness, and prestressing possibilities make stressing cement a valuable binder for prestressed construction.

Theories of chemical action are presented, and research developments are discussed. Methods of producing self-stressed piping are described and compared.

Résumé

Le ciment expansif et imperméable soviétique a été développé en 1942. On l'obtient par brouage à sec de ciment alumineux, de gypse, et d'hydrocalumite artificiel (C_4AH_{13}). Son fonctionnement est basé sur la formation rapide de sulfoaluminate à forte teneur en sulfate (ettringite). Il développe rapidement une haute résistance, fournit la compensation complèt de retrait, une dilatation suffisante, et une forte étanchéité à l'eau. Il est d'un usage excellent dans la réparation et la restoration de constructions en béton, et comme couche imperméable.

Le ciment soviétique autocontraint est d'un développement plus récent, et continue à faire l'objet de recherches. Il a trois composants: du clinker de ciment portland finement broyé, du ciment alumineux, et du gypse. Des pourcentages typiques sont: 66:20:14 quand le ciment portland est d'une teneur en C_3A modérément élevée. L'utilisation d'un dosage peu élevé en eau (25–30%) dans le mortier 1:1 donne de bons résultats avec un traitement hydrothermique (jusqu'à 100 °C) après un jour de durcissement naturel. Le sulfoaluminate à faible teneur en sulfate se forme d'abord. La recristallisation en sulfoaluminate à forte teneur en sulfate dans la masse déjà durcie cause la dilatation, en maintenant l'adhérence à l'armature d'acier, causant ainsi la contrainte de ce dernier. À cause de sa haute resistance, son étanchéité à l'eau et ses possibilités de précontrainte le ciment autocontraint se trouve un liant valable pour les constructions précontraintes.

Les théories de l'action chimique sont présentées, et le développement des recherches est discuté. Les methodes de production de conduites autocontraintes sont décrites et comparées.

Zusammenfassung

Der in der Sowietunion hergestellte wasserfeste Expansivzement, wurde im Jahre 1942 entwickelt. Man erhaltet ihn durch trockenes Vermahlen von Tonerdezement, zusammen mit Gips und synthetischem Hydrokalumit (C_4AH_{13}). Das Benehmen einer solchen Mischung muss durch die schnelle Bildung des hoch sulfathaltigen Sulfoaluminats (Ettringit) erklärt werden. Dieser Zement entwickelt seine höchste Festigkeit schnell, zeigt vollständige Schwindungskompensation, hat eine genügende Ausdehnung und ist in hohem Grade wasserdicht. Man kann ihn gut für Reparaturarbeiten und Wiederherstellung von Betonkonstruktionen gebrauchen, und auch als wasserbeschützende Auflage.

Der in der Sowietunion hergestellte Spannungszement wurde viel später entwickelt; die Forschungsarbeiten sind noch im Gange. Drei Bestandteile sind darin enthalten: Feingemahlener Portlandzementklinker, Tonerdezement und Gips. Eine typische Prozentanalyse zeigt 66:20:14, wenn der darin enthaltene Portlandzement einen ziemlich hohen C_3A-Gehalt hat. Der Gebrauch von nur wenig Wasser (25–30%) in dem 1:1 Mörtel zeigt gute Erfolge bei der nassen Wärmebehandlung (bis zu 100 °C) nach einem Tage natürlicher Erhärtung. Zuerst wird ein Sulfoaluminat gebildet, mit einem niedrigen Sulfatanteil. Die Umkristallisierung zum hochsulfathaltigen Sulfoaluminat, nachdem die Masse schon hart geworden ist, bringt eine Ausdehnung hervor, und die Verbindung mit der Stahleinlage

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the U.S.S.R. Academy of Construction and Architecture, Moscow, U.S.S.R.

ist erhalten, was natürlich zur Folge hat, dass der Stahl gespannt wird. Die hohe Festigkeit, die Wasserdichtigkeit und die Möglichkeit, eine Vorspannung zu erteilen, tragen alle dazu bei, dass dieser Spannungszement ein wertvolles Bindematerial für vorgespannte Konstruktionen darstellt.

Theorien der chemischen Reaktionen werden erörtet, und der Erfolg der Forschungsarbeit wird besprochen. Die Methoden der Produktion selbstspannender Röhre werden beschrieben und untereinander verglichen.

Introduction

The fundamental consideration of engineers, who for many years have been working with no little success, has always been to create cements which bind natural and artificial rock, crushed stone, gravel, and sand, into a hard, strong concrete mass, quickly and reliably. The aim is to produce constant improvement of every available cement. Certain cements, intended to produce waterproof concrete, require special composition—to assure dense mineralogical cement paste and concrete structure. During setting and hardening, cement components are hydrated and acquire new structural forms, accompanied by concrete volume change.

At these changes, the internal stresses in the colloid particles, and between them, appear and are either partially or completely localized. Hence cement paste and concrete undergo uninterrupted volume changes.

Cement paste expansion, in consequence of so-called "inconstant volume", or of the influence of sulfate water, causes cracking, just as concrete shrinkage, highly undesirable, also leads to cracking.

Fargoing research has long been engaged in efforts to eliminate the harmful influence of shrinkage on reinforced concrete, or to provide conditions to obtain setting and hardening without shrinkage. Only in 1942 was this problem basically solved, when Soviet scientists created an expansion cement, now widely applied in construction. This cement is based on calcium hydrosulfoaluminate formation, which has interested many Soviet scientists (Baikov, Budnikov, Moskvin, Kind, Rehbinder, Orlov, Yoong, Yoodovich, Lapin, Kravchenko, Danelian, and others) as well as foreign scientists (Michaelis, Lafuma, Deval, Jones, Biehl, Sestini, Turriziani, Schippa, Wells, Clarke, McMurdie, D'Ans, Eick, Kalousek, Berkley, Lufsky, Klein, Troxell, and others).

Waterproof expansion cement, called WEC (author—V. V. Mikhailov) is a quick setting and quick hardening hydraulic binder, reaching high strength in several hours. This cement successfully withstands high hydrostatic pressure without any signs of water transmission.

WEC is obtained by combined dry grinding of high-alumina cement, gypsum, and artificial C_4AH_{13} (known as the mineral hydrocalumite). The latter is obtained by joint hydration of high-alumina cement and lime, followed by drying and grinding. The degree of expansion of this cement is largely regulated by change in the proportions of components.

Formation of calcium hydrosulfoaluminate $C_3A(C\bar{S})_3H_{32}$* (ettringite), known as "cement bacillus", concrete's most dangerous enemy [1][1] and the cause of considerable concrete building damage, is employed to solve this problem in cement expansion, not only for shrinkage elimination, but also to obtain active expansion. Calcium hydrosulfoaluminate appears in the early stages of WEC hydration and its formation is completed shortly after cement setting. Expansion thus begins and also ends in the short time of the cement paste stiffening, i.e., during the early period and first phase of cement hardening, thereby completely avoiding the harmful influence of ettringite formation.

It was in 1943 that WEC cement first came into use to rebuild war-destroyed reinforced concrete constructions; later in subway construction to replace lead for caulking joints of cast iron tubings, guaranteeing watertightness, high strength, and quick building. WEC cement finds use also in coal pit bracing. Good results were also obtained by expansion cement application in the repair and restoration of underground infiltrated concrete constructions.

To date we have worked out very simple and rapid methods of tamping cracks, holes, and cavities, which immediately stop water filtration, making the construction ready for use.

It is customary to apply waterproof cover as a concrete jacket in underground construction, when shotcreting with WEC concrete greatly simplifies the work.

An isolation layer of a WEC concrete, 3.5 cm thick, can be placed directly on the damp surface, promptly stopping water seepage. Such layers are applied to isolate dam surfaces, hydrostation tunnels and pipes, buttresses, tanks, and other underground and sea constructions. The method is applicable in building repair to restore to proper condition damp or submerged premises.

Thus, Soviet engineers have created a waterproof expansion cement which has become an industrial product, and has overcome the difficulties involved in concrete contraction. Again, this cement is used in various branches of construction to replace lead, metal, and other materials. Creation of this cement is an example of the profitable use of harmful factors in construction building, "cement bacillus" for example, whose formation and structural expansion are connected with the initial period of WEC existence, when the colloidal formation in cement paste is maximum.

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*The symbol $\bar{S}$ is here used for SO_3. The bar distinguishes from $S=SiO_2$.

[1] Figures in brackets indicate the literature references at the end of this paper.

All known cements are now applied only to make strong stone from ballast, gravel, and sand, but these binders have unexplored qualities far beyond present applications.

Cement's "inconstant volume" and the possibilities of regulating nonelastic expansion are as yet not profitably employed. These factors establish a condition in concrete in which the reinforcement becomes extended and prestressed, making unnecessary the mechanical methods now practiced. This novel idea of creating self-stressing, obtainable by the help of stressing cement, opens wide horizons for application in building, and provides economy in materials and expenditure.

It must be pointed out that in world practice there has been very little research on binder compositions which cement by hardening and supplying sufficient energy to deform and stress the reinforcement. Therefore the achievements of Soviet scientists may be considered as the first step towards solving this problem.

Soviet stressing cement (authors—Mikhailov, Litver, and Popov) is a tricomponent binder made from finely ground portland cement, high-alumina cement, and gypsum, taken in optimum proportions. Mixed with a low amount of water, this cement sets and hardens quickly. Cured by hardening under the required hydrothermic conditions, stressing cement acquires sufficient strength and expands, carrying the reinforcement along and thereby creating self-stressed construction. High mechanical strength, watertightness, and prestressing possibilities make stressing cement a valuable binder for prestressed construction, assuring both watertightness and high tension resistance.

Any portland cement (in amounts of 60–70 percent) to which high-alumina cement and gypsum have been added in the proper proportions makes self-stressed cement.

We now turn to our research in expansion and stressing cement (production possibilities), and means of its use in building.

The Mechanism of Setting and Hardening of Portland Cement Binders

In considering the structure of high strength portland cement clinker we distinguish two structural varieties of clinker compound compositions:

(1) portland cement of high alumina content (fig. 1), in which polymineral structures C_3S and C_2S are glued with a glasslike mass of calcium aluminate (C_3A) and some calcium ferroaluminate (C_4AF),

(2) brownmillerite portland cement (fig. 2) in which polymineral structures C_3S and C_2S are glued with a glasslike mass of calcium ferroaluminate (C_4AF) exclusively. Here C_3A is absent.

To stabilize the technical properties and to regulate setting time, the portland cement clinkers are ground with a small amount of gypsum, which can react quickly with the alumina compounds of the clinker in water medium.

Any mixture of portland cement with water, as a result of absorption and chemical dispersion of the cement grains, which are splinters from the mechanical grinding of clinker compounds (fig. 3), disintegrates into separate micro and colloidal particles clearly described by P. A. Rehbinder [2]. Such a dissociation is accelerated by high solubility of alumina and ferroalumina glasslike matrix compounds and outwedging water action (Rehbinder), owing to penetration into numerous microcracks of cement splinters. As a result, active surfaces of cement grains quickly increase and hydration and hydrolysis are accelerated. Special investigations (A. Smirnov) with the application of radioactive isotopes have shown that 1 hr after mixing of C_3A with water (fig. 4), the active surfaces of cement increase from 3,000 to 300,000 cm^2/g, or by a hundred times. The explanation of these dissociations is that in chemical and mechanical processes cement particles less than 10 μ disintegrate fully into particles of colloidal size (0.1 to 0.01 μ), and form colloidal cement glue. Larger cement splinters of polymineral structure C_3S and C_2S, cannot fully dissociate even over a long time and always retain kernels of cement splinters, untouched by water. The cement glue layer, when the quantity of colloidal formation increases by new colloidal particle absorption, gives a saturated solution, and hydrated crystallization occurs directly around the remaining cement kernels, separated from the former by water diffusion layers, free of soluble salts. In the process of further dissolving, new hydrated ions and molecules of clinker salts are continuously ejected through this layer and are concentrated in the area of colloidal structure of hardened cement paste and are absorbed by the nearest crystalline hydrated formation. The hardened cement paste forms structures where the former cement, new formation, free water, and air are reacting [3]. The role of the latter is also important because hydration speed and volume change, which continuously accompany the structure changes, largely depend on the air distribution in the structure. A schematic drawing (fig. 5) shows the hardened cement paste structure, conditionally, after the alumina compound formations are fully hydrated, which requires little time. By this time, C_3S, and to a small degree C_2S kernels, decrease by hydration from the surface. As the hydration process of C_3S kernels develops, the water diffusion layer diminishes and the process slows down and finally stops because of water

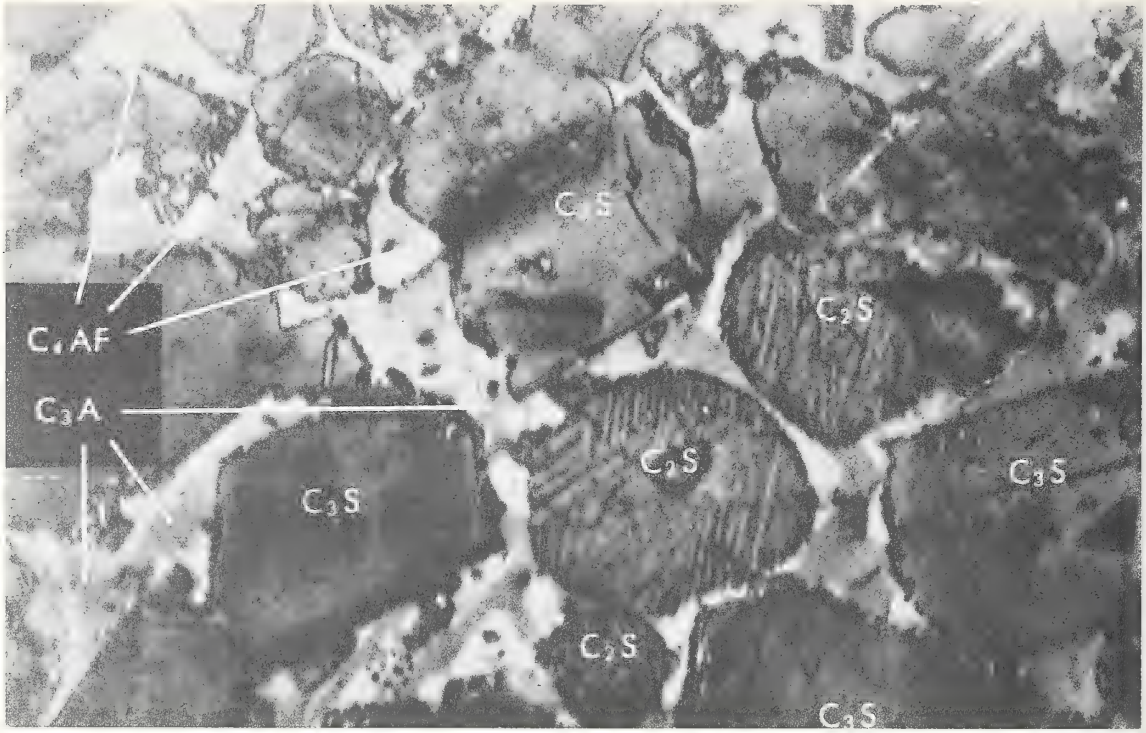

FIGURE 1. *High alumina portland cement structure, rich in* C_3A *and* C_4AF.

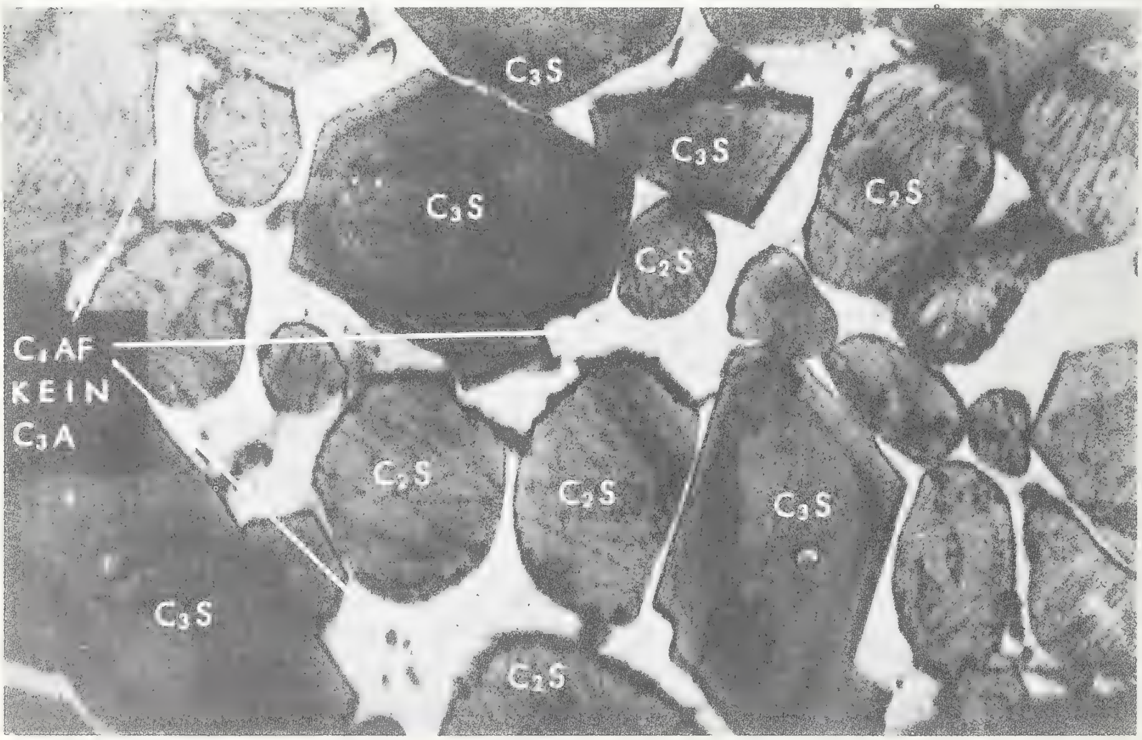

FIGURE 2. *High alumina portland cement structure,* C_3A*-free.*

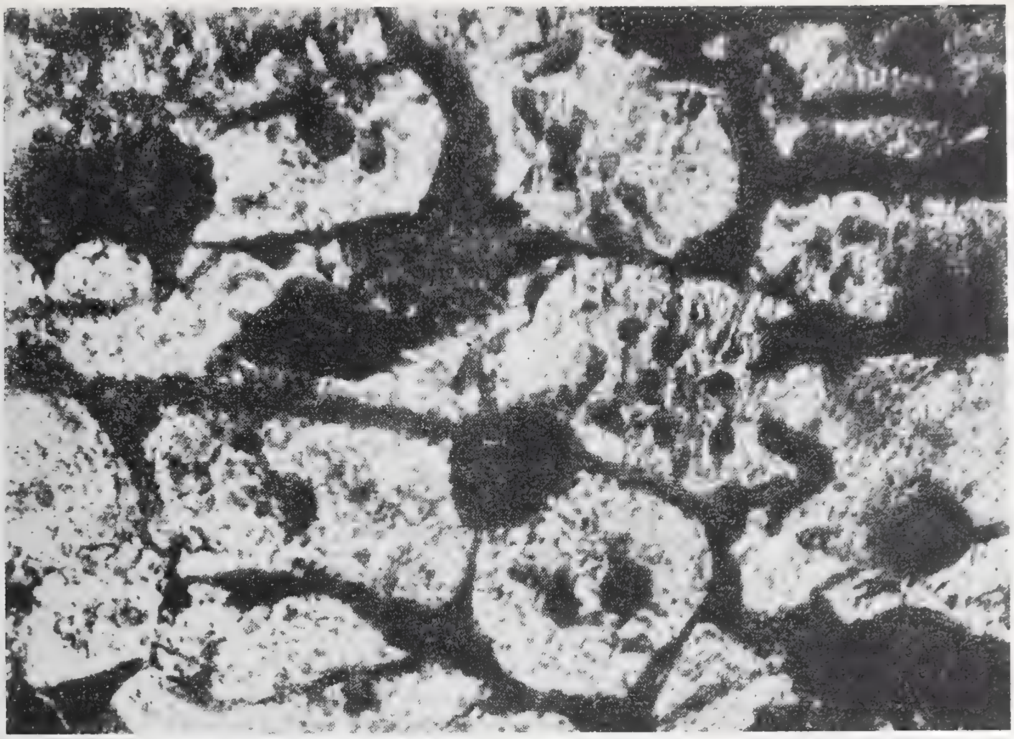

FIGURE 3. *Polymineral structure of portland cement grains.*
Published by Prof. A. A. Baikov.
Enlargement 350 times.

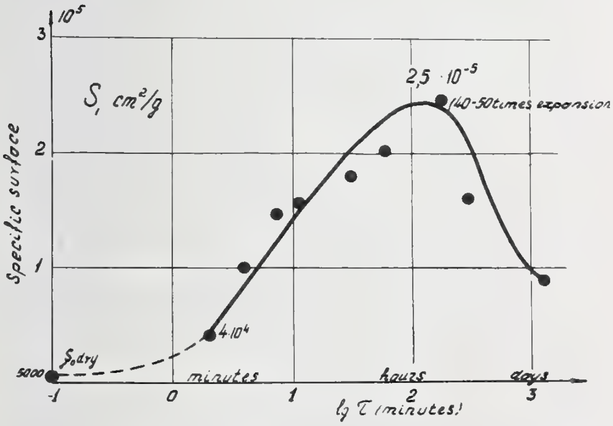

FIGURE 4. *Diagram of cement grain active-surface increase during first hydration period.*

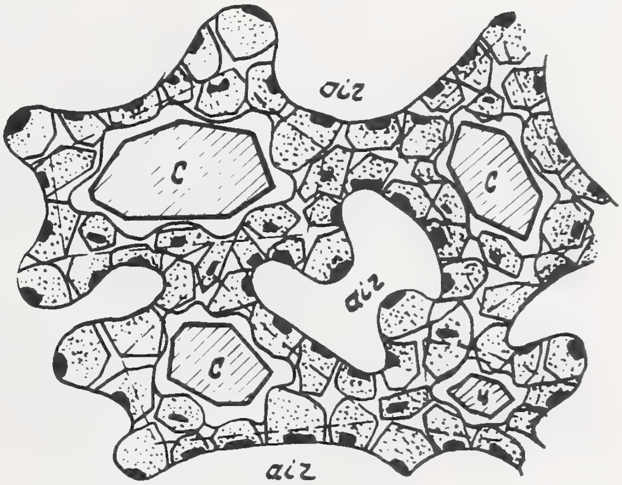

FIGURE 5. *Scheme of gel and air distribution in hardening cement paste.*

deficiency. The more air bubbles, large and small, spread through the structure, the quicker is the development of solution saturation and new crystallization. N. V. Mikhailov [4] has shown in his research on cement hydration the existence of two stages of structure formation:

(a) the stage of formation with predominance of thixotropic coagulation structure, with reversible recovery after mechanical destruction, and

(b) the stage of strengthening, characterized by both crystallization and coagulation structure.

These two stages are definitely distinguished by the change of plastic properties of the cement paste, and are established by continuous and regular tests with a plasto-viscosimeter (method of N. Mikhailov and E. Kalmikova) [4]. For every kind of cement paste there exists one distinctive point (fig. 6) when the plastic strength of structure increases quickly.

In the coagulation structure, soon after its formation, the processes of calcium hydroaluminate crystallization proceed quickly with unusual formation of crystalline needles and chains, which

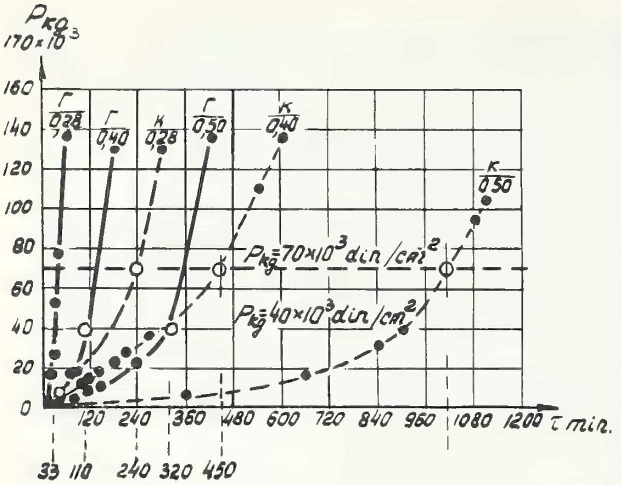

FIGURE 6. *Changes of cement paste plastic strength with time, for different cements and different water contents.*

pierce the coagulation structure of the slow hardening hydrosilicate components like a framework. After the cement paste colloidal phase reaches maximum saturation of new formations, these structures are thickened and completely form such a pseudocrystalline framework.

Maximum saturation is characterized by a breaking point in the diagram (fig. 6), which exactly divides the different states of cement paste structure.

By cement setting and hardening, ions of hydrated clinker salt are ejected to the more distant solution zone, free of hydrated salt influence. Movement of these ions becomes more difficult, the more bubbles, big and small, in this solution (fig. 5). During the first stage, ions of calcium, alumina, and ferroalumina clinker salts predominate, to which later calcium silicate ions are added. Very soon, particularly with low water content in the mixture (hard paste consistency), oversaturation of solution is attained and crystallization begins, giving compounds of new formation, gluelike in appearance, and different in form and configuration. Then the process of crystallization accelerates, following partial water release, with absorption on the new formation surfaces.

As a result of permanent water exhaustion in the direction of nonhydrated clinker kernels, the new formations, in crystallization and coagulation states, are in permanent compression. Particles of these formations draw together (fig. 7), because of molecular attraction in the zones of capillary particle contacts.

Surface capillary tension in these contacts also draws the particles closer. The equilibrium now depends on the capillary forces which attract the structural particles and simultaneously push the particles away. Later these forces not only act spontaneously but also through the thin layer of the water jacket covering the particles.

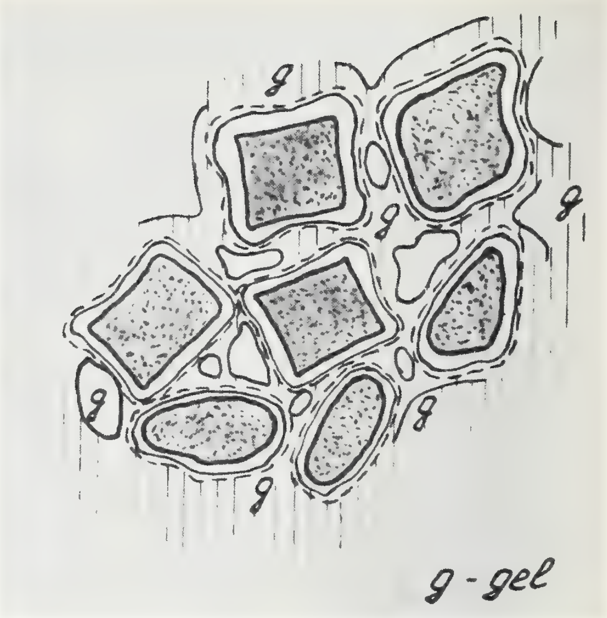

FIGURE 7. *Scheme of hardening cement structure.*

Water molecules which have lost their mobility and are attached to particles by attraction forces due to the tensioning influence between the particles are gradually squeezed out from the contact and packed densely, often replacing by direct molecular interaction new hydrated particle formations. As a result chains, needles, rods, and friable splines of colloidal new particle formations appear and unite or connect by molecular cohesive forces. During C_3S and C_2S hydration, water exhaustion of their kernels causes difficulties, thins the free water layer and finally stops the clinker salt hydration long before expending all the salt reserves. To a certain extent, external water feeding can prolong hydration, but not for a long time. The central zones of C_3S kernels, and especially C_2S, remain as a permanent clinker salt compound, as has been described by Yoong [5].

If the cement paste structure had no air bubbles, each cell between cement grains (generally three) would be filled with water and with hydrated ions of clinker salts, forming only one dimension of crystal, which could freely move in this cell because there is nothing to prevent free transfer in the stream of thermal molecular movement.

If the cement paste cells are air filled (fig. 5), ions may be ejected to the boundary "cement glue—air", and, as a result, along the whole boundary of this cell the possibility exists of forming a great number of crystalline centers, and, in this area, very dense and dispersed cement paste structures arise. These consist of a ramified network of hydrated alumina and ferroalumina compounds, filled (to overflow) with hydrosilica structures. Some scientists [6] affirm that with the hydrosilica formation a crystal of large dimension cannot grow when water content is low, with which we absolutely agree. But this refers only to hardening at temperatures below 100 °C.

When the temperature is over 100 °C, and particularly above 140 °C, even in mixtures with very low water content, calcium hydrosilicate crystallizes in a fibrous network of long lathlike and rodlike crystals known as a tobermorite formation [7], which explains the high mechanical strength of the cement paste in question.

The Soviet method of concrete vibropressing [8, 9] followed by hermetic concrete curing at 140–150 °C in the pressed state, aims to attain strong tobermorite structure quickly. It has already been pointed out that in the state of structure formation, cement glue consists chiefly of alumina and ferroalumina hydrated clinker compounds, which form sufficiently developed fibrous splines and framework.

This structure itself cannot play any important role in cement paste strengthening, but can to a considerable extent insure uniform distribution of hydrated silicate in the whole volume of cement glue, preventing large particles from growing, and providing future high strength of cement paste.

Future cement paste strength can be further increased by repeatedly destroying these cement paste formations by mechanical influences, for example, vibration. In this case there is demolition of many fibrous framework ties which are immediately restored, but in dense structure. During this restoration calcium hydrosilicate crystallization takes place, giving very dispersed and strong cement paste structure. It was on this principle that methods of vibromixing, vibropunching, vibropressing, etc., were developed.

When the alumina and ferroalumina crystalline hydrated formations predominate in cement paste structure, it is possible by varying the amount of water, and by mechanical coercion, vibration and thermal curing to build and rebuild cement paste structure to attain maximum strength.

Shrinkage and Swelling of Cement Paste. Cause of Concrete Watertightness

During the setting and hardening of many known cements, the volume of materials decreases, because of more dense placing of hydrated clinker salts than cement grains plus free water.

Therefore the primary cement paste volume $(C+W+A)$ decreases its volume by hydration to

$$[C+W+A-(1-K)(C_h+W_h)] \qquad (1)$$

where C_h=the original volume of the amount of cement that reacted, W_h=water volume for this hydration, A=air volume, K=ratio of the specific volume of the hydrated product to the original specific volume of the mixture of cement and water that reacted.

Equation (1) shows that by hydration the concrete volume undergoes chemical shrinkage, since $K<1$. There is also physical shrinkage by loss of free water, W, in dry air. Chemical shrinkage is large, and it appears chiefly in volume change during setting and during the first hours of cement hardening. For example, the high-alumina cement paste shrinkage in 1 day is 0.7 percent of primary length, and for portland cement paste 1 percent. Shrinkage is also large if cement paste is water-hardened, causing difficulty during hole and cement joint tamping. Later, by dry storage, physical shrinkage develops as cement paste dries. In wet storage, swelling appears and the volume of cement paste increases.

When the liquid phase of hardened cement paste is in equilibrium with air moisture, no volume change in cement paste occurs.

The interaction between the colloidal formations of cement paste is regulated by cohesive forces of capillary contact (fig. 8). The theory of capillary contact, worked out in 1941 [3], shows that this interaction is determined by free water surface curvature in capillary contacts between new cement paste formations and is described as

$$r_1=\sqrt[3]{\frac{3V}{4\pi\alpha}\left(1+\sqrt{1-\frac{\pi x^3}{3\alpha^2V}}\right)-\frac{x^3}{8\alpha^3}}+\sqrt[3]{\frac{3V}{4\pi\alpha}\left(1-\sqrt{1-\frac{\pi x^3}{3\alpha^2V}}\right)-\frac{x^3}{8\alpha^3}}+\frac{x}{2\alpha} \qquad (2)$$

and the interaction forces as

$$K=\frac{\pi\gamma}{4}\frac{r_1}{r^2}\left(\frac{1}{\frac{\alpha}{2}+\frac{x}{2r_1}}-1\right) \qquad (3)$$

where V=water volume in contact, α=inclination angle of sharp contact side, x=distance between firmly attached colloidal particles, without taking into account water layers, r_1=working diameter of capillary contact, r=average particle dimension, to determine the number of particle contacts in unit surface, γ=surface tension of water.

The cement paste system, under these interaction forces, is always in a state of external compression, constantly changing value when the surrounding air humidity changes. The change of this compression in structure causes cement paste volume changes and shrinkage.

Shrinkage can be calculated by eq (4):

$$\lambda_{sh}=\frac{\pi}{4r^2E_c}=\left[\frac{3}{2}\frac{\gamma^2}{1{,}300\ln\frac{1}{\phi}}-3\gamma\sqrt{\left(\frac{3}{2}\frac{\gamma}{1{,}300\ln\frac{1}{\phi}}\right)^2+r\left(\frac{2\gamma}{1{,}300\ln\frac{1}{\phi}}\right)}+r\left(2\gamma-x\,1{,}300\ln\frac{1}{\phi}\right)\right]+\Delta x \qquad (4)$$

where ϕ=relative humidity of the air.

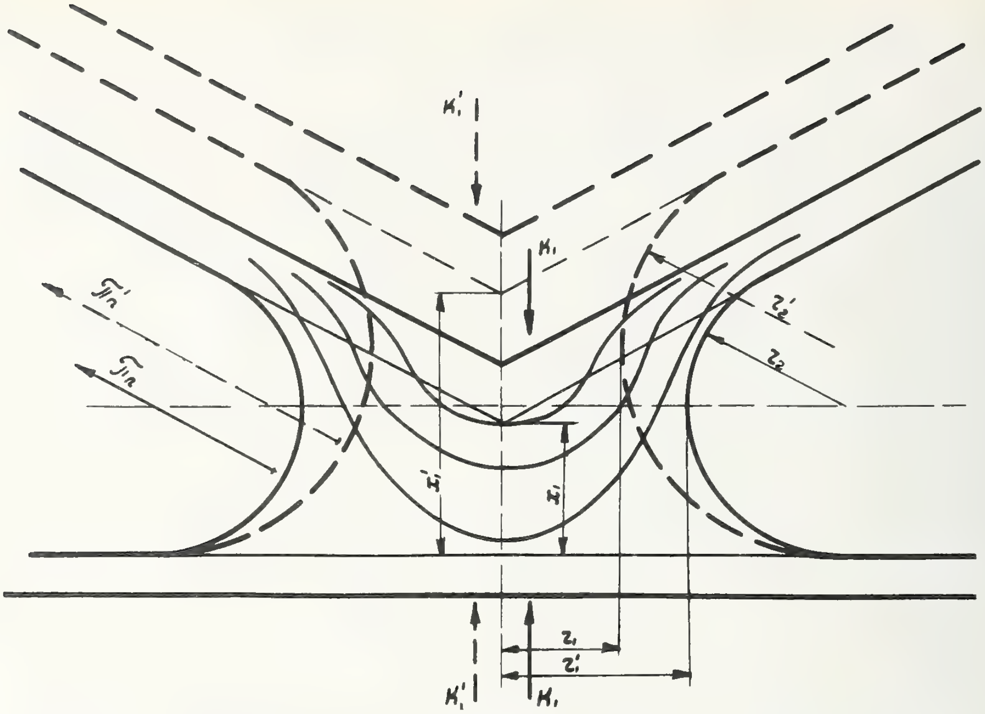

FIGURE 8. *Scheme of coherence of colloidal particles in capillary contact of cement paste.*

Insofar as water exhaustion into diffusion layers and new particle formations and compression by capillary forces develop continuously, in similar manner the average water surface curvature in capillary contacts [3, 10] continuously changes. If at any early moment the humidity of the surrounding air and the water content of the cement paste were in equilibrium, at the next moment, by increasing the humidity, equilibrium disappears and water condensation begins, which relieves the particles' capillary compression, lowering shrinkage. If unlimited humid flow of air is maintained, there is full compensation of shrinkage compression. When hardened cement samples are stored in water, its unlimited ingress produces concrete swelling; but in this case interparticle pores and spaces filled with water increase. If these samples are placed in dry air, cement paste quickly loses water from the large pores, and gives higher shrinkage than in the normal hardening condition. On the other hand, in dry air from the first moment of cement setting and during hardening, equilibrium is absent, and cement paste loses water the more rapidly the larger the pores of the cement structure. As a result high shrinkage appears, connected with water decrease in the capillary contacts. With very dry air and large pores, water loss is so rapid that cement hardening may completely stop. This water loss is accompanied by a high shrinkage (physical factor). The importance of sufficient water retention, especially during the time of setting and first period of hardening, is clear.

TABLE 1. *Technical code for waterproof expansion cement—WEC*

No.	Qualities	Measurement data
1	Stable volume changes	By water setting and warm testing; no volume change.
2	Setting time:	
	(a) Initial set, not before	4 min.
	(b) Final set, not later than	10 min.
3	Grinding fineness:	
	(a) Residue on screen No. 200, not more than	12 percent.
	(b) Passed through screen No. 90, not less than	75 percent.
4	Compression strength, not less than:	
	(a) Cubes 20 x 20 x 20 mm made with cement paste of normal plasticity, water-stored 1 hr after mixing:	
	Age:	
	2 hr	---.
	6 hr	75 kg/cm².
	3 days	300 kg/cm².
	28 days	500 kg/cm².
	(b) Prisms 31.5 x 31.5 x 100 mm, made with mortar of normal plasticity, 1:2 (by weight), stored 1 hr after mixing:	
	Age:	
	24 hr	120 kg/cm².
	3 months	200 kg/cm².
5	Elongation of 31.5 x 31.5 x 100 mm prisms made with cement paste of normal plasticity:	
	(a) Dry-air-stored and tested at age of 1 day, not less than	0.05 percent.
	(b) In water after 1 hour and tested at age:	
	1 day, not less than	0.2 percent.
	28 days, not more than	1.0 percent.

Cement paste in normal storage after long water storage gives greater shrinkage than cement paste with initial curing in air.

Cements are applied in structures as mortar or concrete. The external effect of shrinkage is less than in pure cement, because of aggregate resistance. But the degree of cement paste shrinkage in the cells between aggregates is the same; therefore in the cement paste structure high tensile stresses arise, which can result in microcracks. Microcracks permit water seepage which penetrates through the concrete, not only by applied pressure, but easily because of its own weight. The consequences of cement shrinkage are seen in cases of cement repair of filtrated cracks and holes when the cement paste cracks, or the cracks appear on the hole edge. Invisible microcracks can easily be seen when filtration begins at once upon application of water pressure.

WEC application provides full shrinkage compensation and sufficient expansion. WEC technical properties are given in table 1 [15].

Lab testing of WEC must be done in definite sequence, differing considerably from the ordinary cement testing. It must be remembered that WEC storage and transportation is permitted only in hermetic packing. WEC technical data must be controlled monthly.

Structure of Products of Combined Hydration of Calcium Aluminate Salts, Lime, and Gypsum. The Conditions of $C_3A(C\overline{S})H_{12}$ Formation. Its Stability and Manner of Recrystallization

Former investigations of calcium silicate and aluminate products of cement hydration have analyzed new cement paste structure formations. But such research gives a picture only of the hydrated system with high water content.

Furthermore, the newest technique of concrete production uses less water in concrete, with the result that the structure formation develops differently.

We can affirm that cement hydration with low water content gives quite new formations hitherto unknown. In this connection, we also worked out new methods that influence structure formation. Finally we were able to externally affect structure-building processes and deliberately conduct and change them.

This rebuilding presents large-scale possibilities, still untouched, to obtain new cement paste structure forms.

Broad research by famous scientists in the direction of studying cement paste structure and the mechanisms of their formation and growth, by petrographic microscope, electron diffraction, and electron microscope give no results. This is because these methods cannot test and study the processes of hydration of cement with low water content.

At times this confuses the researcher since the conditions do not correspond to reality.

Difficulties increase because the influence of cement paste structure formation is operative not only at the time of setting, in the first minutes and hours of cement hardening, but at any other time when the original cement paste structure is sufficiently formed and strengthened.

Defects of all microscope methods of cement paste structure analysis result from the manner of sample preparation with high water content, when the required structure form does not appear, or of sample preparation by paste grinding, rubbing, and surface polishing of hardened cement paste, when the structure studied completely disappears or basically changes. Therefore for microscopic analysis we applied special microphotographic methods with very thin nondisturbed cement paste samples which were hydrated on glass (method of Yoong [5]). The feature of this method is in fine cement grinding, with hydration on a glass plate with a low quantity of water, placing on the glass in a very thin layer and pressing with the glass cover to spread the paste. Some samples are then hermetically isolated by glue or paraffin. Thus we obtain nondisturbed cement paste samples, which are stored in dry air, humid air, and water.

It must be said that this method, though only qualitative, answers the questions: Has the structure the formations we are looking for? When do they appear or disappear? Positive advantages of this method of analysis are the possibility of prolonged and continuous optical study of all changes which occur in structure formation, and the possibility of protecting hydrated compounds from carbonation (by CO_2 in air).

Studies by Danelian on high-alumina cements with various compositions gave the following average chemical content:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition
12.3	44.3	4.5	35.0	1.4	1.9	0.60

This cement consists chiefly of CA and low quantities of C_2S and C_2AS. Immediately after mixing it gives a hexagonal structure rich in crystalline water—C_5AH_{34}, with index of refraction 1.487–1.480.

Table 2 gives structural formations and strength of high-alumina cement paste hydrated at 0.3–0.4 water cement ratio, and stored in dry air, humid air, and water.

Hexagonal formations of C_5AH_{34} and C_2AH_8 appear in dry storage, but are unstable and soon disappear, recrystallizing into forms of the low-calcium CAH_{10}. The strength does not increase with time, and remains at a low level, about 250–300 kg/cm^2.

Hexagonal forms C_5AH_{34} and C_2AH_8 which are more stable appear in humid and water storage. Here cement paste strength reaches 950 kg/cm^2 at the age of 1 yr.

Specimens hardening in water give a similar picture. Here new forms with 1.480–1.498 light

TABLE 2.—*High-alumina cement*

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated cement formation.	Air	C_5AH_{34}	C_2AH_8	C_2AH_8	C_2AH_8 C_5AH_{34}	CAH_{10} C_5AH_{34}		1.470–1.498
	Humid air	C_5AH_{34}	C_5AH_{34}	C_5AH_{34}	C_2AH_8 C_5AH_{34}	C_2AH_8 C_5AH_{34}	C_2AH_8 C_5AH_{34}	
	Water	C_5AH_{34}	1.519–1.534	C_2AH_8 C_5AH_{34} C_4AH_{13}	C_2AH_8 C_5AH_{34} C_4AH_{13}	C_2AH_8 1.480–1.498 C_4AH_{13}	C_4AH_{13} 1.477–1.498	C_2AH_8 1.461–1.468 C_4AH_{13}
Compression strength, kg/cm²	Air	256		372	370	321		250
	Humid air	640		810		951		
	Water	761		941	966	943		

refraction, which can be attributed to C_3AH_{18}, are visible. This structure differs from those of the new formations brought about by alumina cement hydration in suspension, when the products of hydration are C_2AH_8, C_4AH_{13}, and C_3AH_6, depending on lime content.

The hexagonal forms C_2AH_8 and C_4AH_{13} were very definite in investigations of water storage samples. These structures can be described as alternations of hydroxyl layers: C_2AH_8—as $2Ca(OH)_2 \cdot 2Al(OH)_3 \cdot 3H_2O$; C_4AH_{13}—as $2Ca(OH)_2 \cdot Al(OH)_3 \cdot 3H_2O$.

All hexagonal calcium hydroaluminates, as is known from the literature, have a family likeness in electron diffraction. C_2AH_8 has a tendency after a time to dissociate into C_4AH_{13} and AH_3 by the reaction:

$$2Ca(OH)_2 \cdot 2Al(OH)_3 \cdot 3H_2O \rightarrow 2Ca(OH)_2 \cdot Al(OH)_3 \cdot 3H_2O + Al(OH)_3$$

but the layer structure does not break, only one layer of $Al(OH)_3$ attains the amorphous state.

Hydroaluminate attains high lime content formation, C_4AH_{13} in the main, when the lime content is high, which results from alumina cement hydrated together with lime.

All hexagonal calcium hydroaluminate formations become unstable and recrystallize in the cubic form, C_3AH_6. Hexagonal formation in hydration at high temperature has never been seen when gypsum is absent. It is different when cement is hydrated together with gypsum. In this case hexagonal forms are quite stable at normal and high temperature. Gypsum immediately reacts with C_4AH_{13}:

$$C_4AH_{13} + 3(C\overline{S})H_2 + aq = C_3A(C\overline{S})_3H_{32} + CH + aq.$$

By insuring contact with water the formation of $C_3A(C\overline{S})_3H_{32}$ quickly ends. It appears in the form of lathlike rods at low lime concentration and in form of thinnest needles at high lime concentration. Gypsum binding in $C_3A(C\overline{S})_3H_{32}$ is accelerated by adding C_4AH_{13}.

Table 3 gives the structure formation, strength data and volume changes of WNC cement paste samples hydrated at 0.3–0.4 water-cement ratio, and stored in dry air, humid air, and water.

TABLE 3. *Tricomponent waterproof cement WNC*

Alumina cement—75 percent by weight
Gypsum ($CaSO_4$ $0.5H_2O$)—6.25 percent by weight
Artificial hydrocalumite C_4AH_{13}—18.75 percent by weight

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated formation.	Air	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8 C_4AH_{13} AH_n	1. 489–1. 504 1. 498–1. 504		1. 498–1. 504
	Humid air	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8 C_4AH_{13}	
		$C_3A(C\overline{S})_3H_{32}$	$C_3A(C\overline{S})_3H_{32}$	$C_3A(C\overline{S})_3H_{32}$	$C_3A(C\overline{S})_3H_{32}$		$C_3A(C\overline{S})_3H_{32}$	
	Water	1.510–1.528 CAH_{10}	1.522–1.537 1.486–1.195	1.519–1.528 C_2AH_8	C_2AH_8 $C_3A(C\overline{S})_3H_{32}$	C_2AH_8 $C_3A(C\overline{S})_3H_{32}$	C_2AH_8 $C_3A(C\overline{S})_3H_{32}$	
Compressive strength kg/cm².	Air	207		200	202	235		
	Humid air	210		343	340	377		
	Water	210		275	380	430		
Elongation (+) or shrinkage (−).	Air	−0. 08	−0. 16	−0. 18	−0. 22	−0. 22	−0. 47	−0. 47
	Humid air	−0. 05	+0. 02	+0. 12		+0. 49	+0. 40	
	Water	+0. 08	+0. 09	+0. 15	+0. 33	+0. 40	+0. 31	

Cement WNC is a variety of WEC, but with lower gypsum and higher C_4AH_{13} content. It gives little expansion in humid storage and is called waterproof nonshrinking cement.

This cement is characterized by quick setting, quick hardening, and instantaneous watertightness.

Due to this property, WNC is applied for caulking strongly filtrated cracks, holes, cavities, etc.

Table 3 shows that WNC, after mixing, gives hexagonal formations C_2AH_8 and $C_3A(C\overline{S})_3H_{32}$ at once. On the third day of hardening, the high-lime formation C_4AH_{13} does not appear, because of the latter's quick reaction with $C\overline{S}$ with formation of $C_3A(C\overline{S})_3H_{32}$, showing light refraction of 1.464–1.458, but only in the case of humid and water storage. In dry storage no traces of $C_3A(C\overline{S})_3H_{32}$ are found. In long storage (over 360 days) crystals of gypsum were continuously present.

WNC strength is low (a characteristic of this cement). It is 50 percent of normal high-alumina cement strength in humid storage, and only 25 percent in dry storage. But despite this, WNC is indispensible when there is destruction to repair.

The process changes basically by adding lime to high-alumina cement instead of artificial hydrocalumite C_4AH_{13}, when gypsum is present. C_2AH_8 and C_4AH_{13} formations then appear, react with gypsum, and form calcium sulfoaluminate, now as a "low sulfate" structure—$C_3A(C\overline{S})H_{12}$ with light refraction 1.489–1.504 and chain-connected hexagonal plates. When lime is present and the water content limited, at first hydration results only in the "low sulfate" structure, formerly unknown. But this formation is unstable, and with gypsum present and high water content, recrystallizes into the "high sulfate" structure of calcium sulfoaluminate—$C_3A(C\overline{S})_3H_{32}$—with intensive expansion.

$C_3A(C\overline{S})H_{12}$ has plate structure, similar to hexagonal calcium hydroaluminate, and its formation does not lead to expansion.

Table 4 gives new structure forms and light refraction, specimen strength, and volume change for high-alumina cement, gypsum, and lime hydrated together in the proportions 88:4:8 at 0.3–0.4 water content, and stored in dry air, humid air, and water.

At 3 days C_2AH_8 and $C_3A(C\overline{S})H_{12}$ are found in all samples, as well as at 14 days. Later, $C_3A(C\overline{S})H_{12}$ disappears in air-stored samples, but C_2AH_8, C_4AH_{13} and gypsum are present. Test specimens show shrinkage which reaches 0.44 percent at 270 days. C_2AH_8 and $C_3A(C\overline{S})H_{12}$, in humid air and water-stored samples were stable at 3 days, but at 28 days, the water-stored samples showed the high sulfate structure of calcium sulfoaluminate, and expansion was 0.73 percent, causing cracking. Gypsum crystals were also very plainly seen. At 180 days "low sulfate" structures disappear because of complete recrystallization into the "high sulfate" form. Expansion reaches 2.47 percent, cracks open wide, and gypsum disappears completely. Because of large expansion, specimen strength is low, and after 1 yr of water storage is 176 kg/cm².

TABLE 4. *Tricomponent waterproof cement*

Alumina cement—88 percent by weight
Gypsum ($CaSO_4 \cdot 0 \cdot 5H_2O$)—4 percent by weight
Lime (CaO)—8 percent by weight

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated cement formation.	Air	1.519–1.528 1.480–1.498 $C_3A(C\overline{S})H_{12}$	C_2AH_8 C_4AH_{13} $C_3A(C\overline{S})H_{12}$	1.480–1.498 1.507–1.528 CAH_{10}	1.480–1.498 1.507–1.528 CAH_{10}	1.480–1.498 C_2AH_8 C_4AH_{13}	----- -----	----- 1.498–1.471
	Humid air	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$
	Water	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$ $C_3A(C\overline{S})_3H_{32}$	C_2AH_8 $C_3A(C\overline{S})H_{12}$ $C_3A(C\overline{S})_3H_{32}$	C_2AH_8 $C_3A(C\overline{S})_3H_{32}$	C_2AH_8 $C_3A(C\overline{S})_3H_{32}$	-----
Compressive strength kg/cm².	Air	191	-----	277	290	313	-----	304
	Humid air	172	-----	215	220	150	-----	167
	Water	182	-----	247	248	179	-----	176
Elongation (+) or shrinkage (−)	Air	−0.08	−0.07	−0.12	−0.24	−0.30	−0.44	−0.31
	Humid air	+0.01	+0.08	+0.23	+0.73	+2.30	+2.45	+2.60
	Water	+0.06	+0.15	+0.26	+0.70	+2.11	+2.47	+2.63

Stressing Cement—SC, Its Nature and Properties (Strength and Expansion)

The use of gypsum was for a time highly recommended as an additive for portland cement to attain rapid hardening and strength increase.

Naturally, this composition did not achieve good results, as the formation of $C_3A(C\overline{S})H_{12}$ and the following slow recrystallization into $C_3A(C\overline{S})_3H_{32}$ led to a drop in strength and sometimes to concrete destruction. This feature was intensively studied in Germany by the Dyckerhoff firm [12], manufacturers of special brownmillerite sulfate-resistant cement which does not increase the concrete volume and is not destroyed when gypsum is added. It differs in this respect from normal cement with a large tricalcium aluminate content, which together with a low water content gives the "low-sulfate" form of sulfoaluminate of calcium, with subsequent destructive recrystallization into the "high-sulfate" form. Considering in this connection two examples of portland cements (see figs. 1 and 2), attention should be paid to the fact that sufficient iron oxide in the cement to a high degree retards the formation of dangerous forms of calcium sulfoaluminate, even in calcium hydroxide saturated media. Complete absence of C_3A is a characteristic feature of this brownmillerite cement, which is why it is not destroyed in sulfate water.

In other countries, scientific thought seeks to counteract the destructive influence of sulfate water by introducing pozzolan into the concrete during mixing. D'Ans and Eick [13], and Eitel [14] have shown that adding pozzolan does not eliminate the formation of calcium hydrosulfoaluminate. It only retarded ettringite formation for weeks and months.

The formation of the "low-sulfate" form of calcium hydrosulfoaluminate proceeds violently, and subsequent recrystallization into the "high-sulfate" form occurs in mechanical mixtures of portland cement, high alumina cement (or other aluminate compounds) and gypsum powders. Thus, a paste mixture of 65 percent portland cement, 15 percent gypsum, and 20 percent alumina cement of normal consistency, stored in water after hardening 2–3 days to a strength of 200–300 kg/cm², rapidly expands, due to the water absorption and "high-sulfate" formation, until it is finally disintegrated into an adhesive finely dispersed mass. This mixture has no hydraulic properties and would appear to be unfit for use. Yet its expansive power is very great. As explained in detail below, such a hardening cement mixture, not immersed in water, does not cause hydrosulfoaluminate recrystallization.

The cement paste in this case expands somewhat on account of the mix water, but is not destroyed. However, if such a cement paste is immersed in water even after 1–2 yr, the recrystallization process is renewed with great force and the system is completely destroyed, forming an adhesive mass.

It is clear that this type of cement cannot ever be used for construction purposes.

Investigating the hardening processes of portland cement clinker mixed with gypsum in various proportions, we noted that, even for small additions of gypsum reacting with C_3A, the formation and recrystallization of calcium hydrosulfoaluminate took some time, longer when water ingress into the system became more difficult.

It is possible to make up the initial combination of components with low water content so that upon isolated storage of the cement paste (without water admission) the expansion stops at a definite age. However, when water is admitted the process is renewed and leads to expansion, which finally stops without destroying the system.

As an example, cement paste of the proportions 14:20:66 (gypsum, high-alumina cement, portland cement) mixed with 30 percent water (fig. 9) may be used. Along the abscissa, days are plotted and, along the ordinate, relative expansion

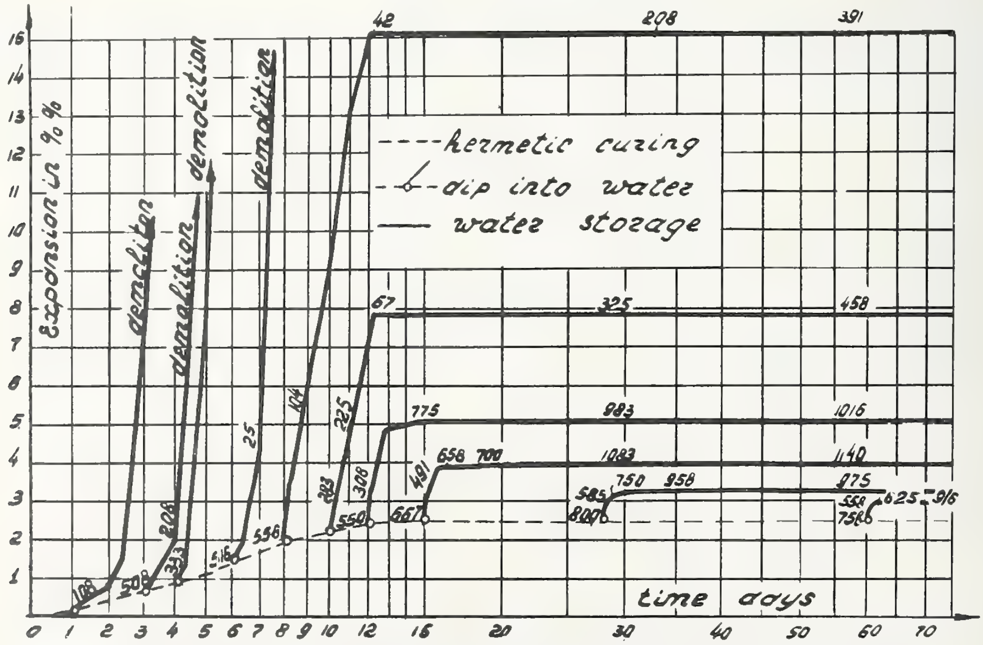

FIGURE 9. *Expansion-strength diagram of stressing cement paste at 200 °C in the isolated state showing changes with time at which immersed.*

of the sample in percentage. The dotted line shows expansion of sample during isolated storage in paraffin-coated foil. At 15 days, expansion is stabilized at a level of 2½ percent. Cement paste strength at this age equals 667 kg/cm^2; after 28 days 800 kg/cm^2. If such samples are taken from isolation on 1, 3, 4, and 6 days and immersed in water, they expand rapidly and samples are completely disintegrated. Samples immersed after 8 days and having at that time a strength of 558 kg/cm^2 showed rapid recrystallization to "high-sulfate" formation, but were not destroyed completely and retained their shape without any signs of cracks. At 12 days, i.e., after 4 days of water storage, the samples had expanded 15 percent (fig. 10) and the strength was only 42 kg/cm^2. However, during further water storage, at 28 days the strength reached 208 kg/cm^2, and at 60 days, 391 kg/cm^2. Samples immersed after 10 days, with strength of 560 kg/cm^2, had expanded 8 percent at 12½ days, and the strength had dropped to 67 kg/cm^2, but with further water storage a strength of 458 kg/cm^2 was attained at 60 days.

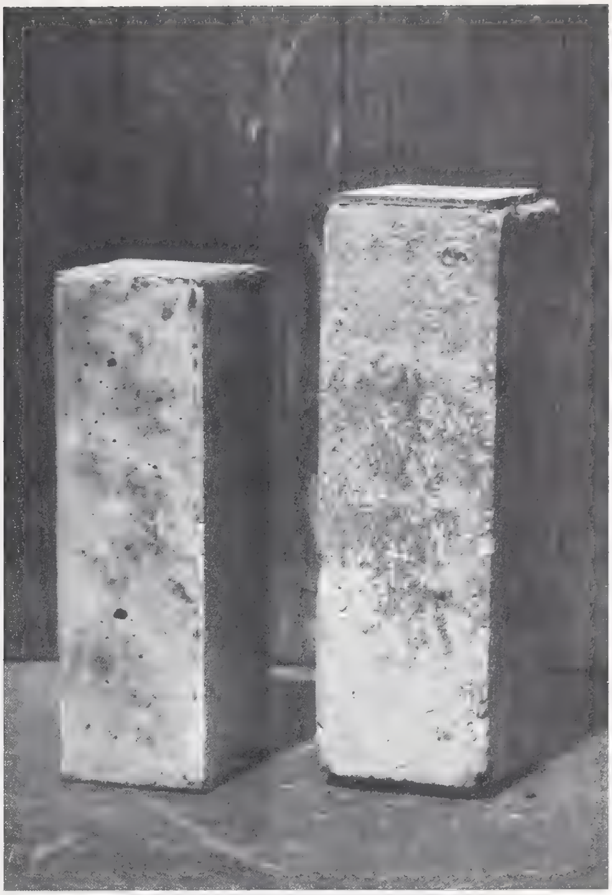

Figure 10. *View of SC hydrated specimen with 15 percent elongation, immersed 8 days after isolated storage (see figure 9), in comparison with similar portland cement (nonelongated) specimen.*

For samples immersed after 12 days, the strength, which was then 536 kg/cm^2, dropped temporarily to 308 kg/cm^2 at 13 days, but at 15 days rose to 775 kg/cm^2. The expansion was 5 percent, and the strength continuously increased, reaching 1,016 kg/cm^2 at 60 days.

Similar results were obtained when samples were immersed after 15, 28, and 60 days.

The curve in question shows that, with increase in specimen age at the time when immersion begins, additional recrystallization of the calcium hydrosulfoaluminate occurs by additional water absorption, but in a lower degree and in less destructive form. However, all specimens during the initial water expansion period showed a temporary 30-35 percent drop of strength.

The example mentioned shows that the processes of setting, hardening, and expansion of the tricomponent composition of portland cement, high-alumina cement, and gypsum may be controlled. Later we will show that it is possible to direct these processes by optimum proportioning of components. Henceforth this composition will be called stressing cement SC (see table 5—Technical Code) [16].

Self-stressed cement paste is composed of selected cement paste structure with prearrangement and reorganization of the entire structure during cement, mortar, and concrete setting and hardening processes. Previously, examples of directed interference with cement paste existence and behavior were unknown.

Pure portland cement and high-alumina cement are best applied as clinker, first grinding them for SC preparation. It is advisable that the cement fineness be not less than 3,500 cm^2/g. The tricomponent powders are batched in the vibrating mill for 8–10 min, to uniformity.

At low water mixture (25–30 percent by weight), lime, portland cement, and the CA of the alumina cement dissolve rapidly and a large amount of water is absorbed. Ions of hydrated minerals rush toward the zones of lower concentration of the liquid phase and crystallize, and meeting with gypsum grains they react and form lathlike splines of calcium hydrosulfoaluminate on gypsum grain surfaces.

The plastic strength of the system rapidly increases, beginning 2–3 min after mixing.

The saturation with calcium hydrate, and the limited water phase, hampers the growth of the "high-sulfate" formation $C_3A(C\overline{S})_3H_{32}$ which is limited by formation of a "low-sulfate" product $C_3A(C\overline{S})H_{12}$.

As a result, a branched framework is formed of $C_3A(C\overline{S})H_{12}$, C_4AH_{13}, and $C_3A(C\overline{S})_3H_{32}$ lathlike splines.

The last two needlelike formations are completely intertwined. The higher the water cement ratio at hydration, the more $C_3A(C\overline{S})_3H_{32}$ and the less $C_3A(C\overline{S})H_{12}$ and pure gypsum.

This intertwining is, during the initial period, rather loose, gradually becoming compacted by

TABLE 5. *Technical code for stressing cement* (SC)

(Specifications)

No.	Qualities	Measurement data
1	Setting time:	
	(a) Initial set, not before	2 min
	(b) Final set, not before	6 min
2	Fineness of grinding:	
	(a) Residue on screen, N 02, not over	1 percent
	(b) Passing through screen N 0085, not less than	80 percent
3	Strength of cubes, size 20 x 20 x 20 mm, made of cement paste of normal consistency, should be as follows:	
	(a) For specimens cast 18–20 hr at 20±2 °C, not less than	200 kg/cm^2
	(b) For specimens cast 18–20 hr at 20±2 °C and then 6 hr (without molds) in water at 70° C, not less than	450 kg/cm^2
	(c) For specimens given hydrothermic treatment in conformance with § "b" of the given item and then stored in water at 15–20 °C for 24 hr:	
	Not less than	600 kg/cm^2
	Not less than	850 kg/cm^2
4	Elongation of prism, size 31.5 x 31.5 x 100 mm, made of cement paste of normal consistency, given hydrothermal treatment according to the sequence described in § "b", should be at the end of treatment not less than	2. 2 percent
	Elongation of prism during such treatment, in relation to the elongation value at the end of 6-hr thermal treatment, should be:	
	(a) After 2 hr thermal treatment, in the range	75–85 percent
	(b) After 3 hr thermal treatment, in the range	92–97 percent
	Increase of specimen elongation in water storage, in relation to the elongation value at the end of thermal treatment, should be:	
	After 7 days, not over	12 percent
	After 28 days, not over	15 percent
	NOTE: Conformance with requirement of §§ "a" and "b", item 3, and §§ "a" and "b", item 4, is rapid test of SC.	
5	Strength of cubes, size 30 x 30 x 30 mm, made of normal consistency SC mortar (1:1) by weight, should be:	
	(a) For specimens cast 18–20 hours in molds at 20±2 °C, not less than	150 kg/cm^2
	(b) For specimens cast 18–20 hours at 20±2 °C and then 6 hours (without molds) in water at 100 °C, not less than	250 kg/cm^2
	(c) For specimens given hydrothermic treatment in conformance with § "b" of given item and then stored in water at 20±2 °C:	
	After 1 day, not less than	300 kg/cm^2
	After 3 days, not less than	300 kg/cm^2
	After 7 days, not less than	300 kg/cm^2
	After 28 days, not less than	500 kg/cm^2
6	Elongation of prism, size 31.5 x 31.5 x 100 mm, of normal consistency SC mortar (1:1) by weight, should be:	
	At end of thermal treatment (according to § "b", item 5), not less than	0.2 percent
	During further water storage 15-20 °C:	
	After 1 day, not less than	0.5 percent
	After 3 days, not less than	1.5 percent
	After 7 days, not less than	1.8 percent
7	Samples of cement paste of normal consistency mortar (1:1) by weight, during testing (in disks) at the end of thermal treatment should be entirely impermeable at pressure	20 atm

ions and newly formed silicate compounds, which crystallize in the aluminate and sulfoaluminate framework. A feature of crystalline calcium hydrosilicate formation is that, in media with a small amount of water, development rapidly stops, and the growth does not exceed the limits of colloidal dimensions. There is strong competition between all reacting new formations in the cement paste colloidal zone, which quickly leads to exhaustion of moisture resources and retardation of the hydration of the initial cement materials. After about 24 hr of isolated natural hardening (to prevent carbonation of new formations) the strength of the cement paste reaches 200–300 kg/cm^2, and the cement paste coagulation-crystallization structure is characterized by the presence of a highly branched framework of intertwining heavy splines of lath, needle, and lattice-like formations of hydrosulfoaluminate structure and chains of calcium hydroaluminate. The space taken up by these compounds is filled with a coagulation structure of hydrated silicate formations, disintegrated nonhydrated cement kernels, and gypsum grains coated with a solid feltlike shell of $C_3A(C\overline{S})H_{12}$.

SC cement, in a high-water-content mixture, forms $C_3A(C\overline{S})_3H_{32}$ quickly and without interference, because the indefinite number of hydrated ions of CA of high alumina cement and the quantity of C_3A and C_4AF in the portland cement, gradually delivered, rapidly react with the gypsum under conditions of relatively low Ca ion concentration. But the reaction of $C_3A(C\overline{S})_3H_{32}$ formation rapidly ends during the early hardening period when the strength of cement paste is low. In this case there is no noticeable expansion of the system.

Thus, SC with low water mixture supplies the best condition for obtaining in the system the maximum quantity of $C_3A(C\overline{S})H_{12}$, ready for recrystallization.

If such a hardened system is immersed, the cement paste greedily absorbs water and the recrystallization process rapidly converts $C_3A(C\overline{S})H_{12}$ into $C_3A(C\overline{S})_3H_{32}$, with simultaneous expansion of the system, for the process occurs on gypsum grain surfaces, and causes structural rearrangement with water absorption. The $C_3A(C\overline{S})_3H_{32}$ structure is formed on the gypsum grain surface like directed thin needles and presses against the adjacent new formations, disturbing their adhesion. As a result of this growth, the structure is completely demolished and breaks into separate small pieces. This behavior was observed in cement paste specimens (fig. 9), immersed in water after 1, 3, 4, and 6 days of isolated storage. Simultaneously, due to $C\overline{S}$, recrystallization of C_4AH_{13} formation into $C_3A(C\overline{S})_3H_{32}$ occurs.

If expansion of the system during recrystallization is limited to 15 percent, total destruction does not occur, but as mentioned above, destruction of mechanical adhesion between colloidal particles of C_2SH_2 and CSH leads to structural weakening, which, after expansion stops, heals as the result of delivery of ions of hydrated silicates of calcium and the development of new connections. For specimens immersed after 15 days, healing proceeds very quickly, and some weakening is observed only in brief loss of strength.

Destruction of structural adhesion as a result of recrystallization to $C_3A(C\overline{S})_3H_{32}$, and the formation of new connections, may also be directed by shifting the destruction and restoration periods, timing them to the accumulation of new high strength silicate formations, and superimposing them for strength stabilization.

Direct Methods of Expansion and Hardening. Optimum Alumina Compound Admixture. Optimum Hydrothermic Hardening Process. Self-Stressing Mechanism

Hydrothermic treatment of the system is effective for such formerly discussed adjustment.

Through heating, the influence of the hydration of the silicate cement components is highly accelerated. Therefore the reproducing processes are performed rapidly and at a certain temperature do not lag behind the processes of structure destruction. During a definite time, as many and even more connections are restored as are destroyed. Because of this, the strength is either maintained at the fixed level, or even increases on expansion.

Heating of the system makes it possible not only to avoid excessive expansion and destruction of the cement paste, but also permits time decrease for all processes, which, according to the curve (fig. 9), take so long to develop.

Investigations have shown that heating cement paste for 2 hr at 70–80 °C when the strength is about 200–300 kg/cm^2 gives expansion sufficient for the system without any signs of strength drop.

Figure 11 shows data on expansion and strength increase of SC specimens heated at 80 °C for 1, 2, 3, 5, and 7 hr when the initial strength was 200 kg/cm^2. All samples heated 2, 3, 5, and 7 hr expanded 2 percent and reached strength of about 500 kg/cm^2. Further water storage of SC samples did not show more expansion, because the gypsum was fully consumed during the first 2 hr of heating, and all $C_3A(C\overline{S})H_{12}$ was recrystallized into $C_3A(C\overline{S})_3H_{32}$.

However, the strength of the cement paste continuously increased owing to the progress of the hydration of the C_3S and C_2S of the portland cement, leading the system to further densification. Cement paste after 28 days reaches a strength of 1,200–1,300 kg/cm^3. Thus, heating the system for more than 2 hr had no effect in any case. It might be assumed that such hydrothermic treatment during hardening would be selected as best for application in structures; however, with mortar, difficulties were met with. The composition of SC paste, which resulted in an increase of strength accompanying 6 percent expansion during heating, showed a much greater strength drop in mortar, sometimes 2–3 times, making this composition of mortar unfit for self-stressing.

Actually, reinforced concrete self-stressing is possible only when the concrete bond with reinforcement exists and concrete acts as a hard body, deforming identically and simultaneously with the steel. For such reinforcement action, concrete should continuously possess the required strength and density. Insufficient strength due to temporary drop causes plastic concrete flow around the reinforcement, without its significant lengthening. Thus, we obtain large reinforced concrete expansion, but without self-stressing, even though, during further hardening in water storage, the strength is not only restored, but significantly exceeded. This may be because, during the rapid process of SC expansion, cracks arise from the retarding action of the aggregates, which do not increase in volume.

All attempts to prevent the drop in SC mortar strength lead to lower expansion power, and in turn to insufficient self-stressing.

Self-stressing technology has therefore been greatly changed.

Investigations showed that $C_3A(C\overline{S})H_{12}$ recrystallization into $C_3A(C\overline{S})_3H_{32}$, in calcium hydrate media, is retarded by further temperature increase; simultaneously, hydration of C_3S and C_2S is considerably accelerated at the higher tem-

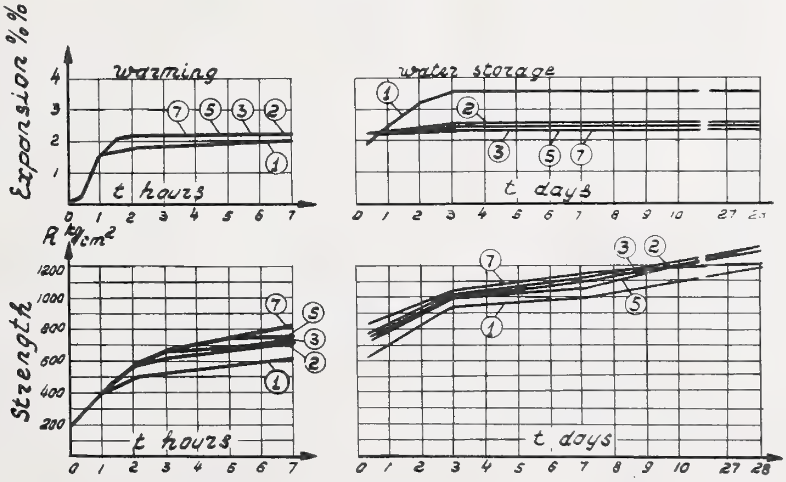

FIGURE 11. *Expansion-strength diagram of stressing cement paste for various durations of water heating, at 80 °C.*

Data in circles show number of hours of heating.

perature. Therefore, the structure destruction period is moved backward, and the period when new connections arise in the process of dissolution and hydration of silicate materials in the cement is moved forward. As a result the following sequence was set for hydrothermic treatment of SC mortar: 6 hr heating in water at 100 °C (boiling water), with initial strength about 160–200 kg/cm². Here mortar expanded very little, with specimen strength increasing to 300–400 kg/cm². During further water hardening, expansion progressed rather evenly, stopping after 3–10 days of water storage.

During expansion, mortar strength either did not change or slightly increased.

In this case the expansion mechanism generally acts, only the process takes several days, giving the hardening of C_3S and C_2S time to heal the recrystallization ruptures which have appeared.

Further experimental work [17] showed that this self-stressing mechanism is the best available, and it was somewhat improved to make the allowed expansion time less than 3 days. Additional investigations were then undertaken. Equipment was built for self-stressing mechanism investigation (fig. 12), which could reproduce elastic resistance of any amount. Each chosen degree of rigid resistance corresponded with a certain coefficient of linear system reinforcement, i.e., reproduced any required percentage of concrete reinforcement.

Prisms of sizes 100 × 31.5 × 31.5 mm and 300 × 50 × 50 mm, with strips embedded at the faces, were selected as experimental specimens. Cylinders with transverse spiral wire coils were also investigated, whereby limited elastic volume expansion was obtained.

The investigations of self-stressing showed that elastic resistance increase against specimen expansion leading to self-stressing variation may be expressed approximately by the following equation:

$$\sigma_c = \sigma'_c \sqrt[5]{\frac{\mu}{0.24}}$$

where σ_c = unknown reinforced concrete self-stressing, in kg/cm² with reinforcement = μ, σ'_c = reinforced concrete self-stressing with $\mu' = 0.24$ percent, μ = concrete reinforcement coefficient.

By investigation, a very important and vital feature of SC structure was found, relating both to theory and practice. For very large free stressing-cement expansion, uniaxial elastic resistance of sufficient intensity decreases expansion

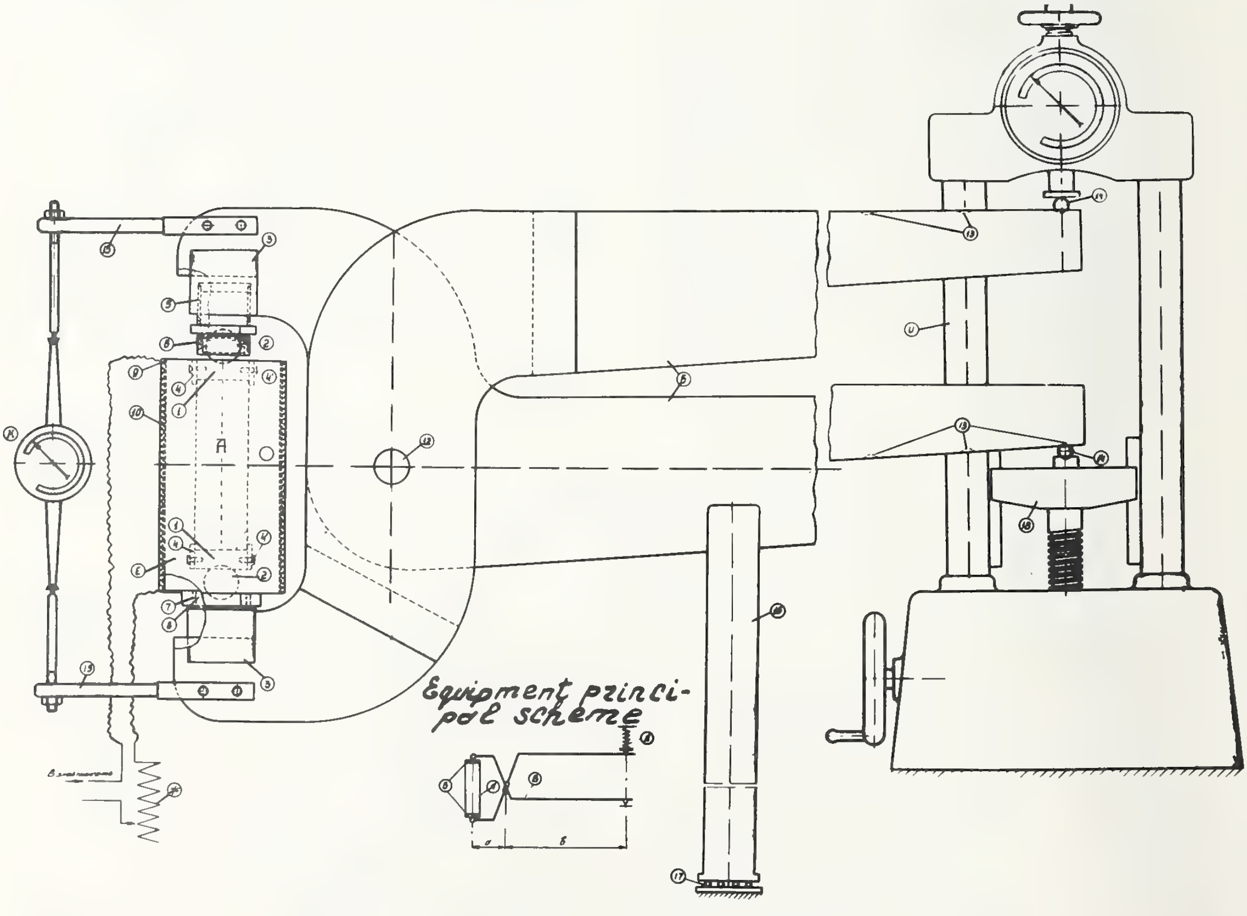

Figure 12. *Measuring instrument for testing cement paste expansion force.*

by over 10 times not only in the direction of action of the resistance but crosswise as well.

This is explained by the strength and volume stability of the system resisting transverse plastic deformations, under uniaxial compression, if cement composition and the hydrothermic sequence of treatment are optimal and there is no drop in concrete strength during self-stressing.

Equipment for investigation of self-stressing power is made to imitate every hydrothermic sequence and all conditions of variable moistening and drying of specimens.

Self-stressing investigations [16] have shown that every portland cement may be employed for production of SC by adding high-alumina cement and gypsum. The only problem is to find the optimal proportioning.

1. If high-aluminate portland cement has rich C_3A content, SC from this cement possesses high expansion, but does not stabilize rapidly.
2. If brownmillerite portland cement is used, without C_3A expansion, SC from this cement stabilizes rapidly, but with less expansion value.

Good results in our experiments were obtained with alite portland cement having the following average mineralogical content:

C_3S	C_2S	C_3A	C_4AF	CaO	MgO	KH
47.02	24.44	12.53	10.46	0.50	4.06	0.864

Using this cement, the SC content proportions selected were 14:20:66, which were checked in comparison with the higher activity SC proportions 18:22:60.

Figure 13 shows the curve of SC strength increase at normal temperature, 22 °C, for storage in isolated conditions under a paraffin layer.

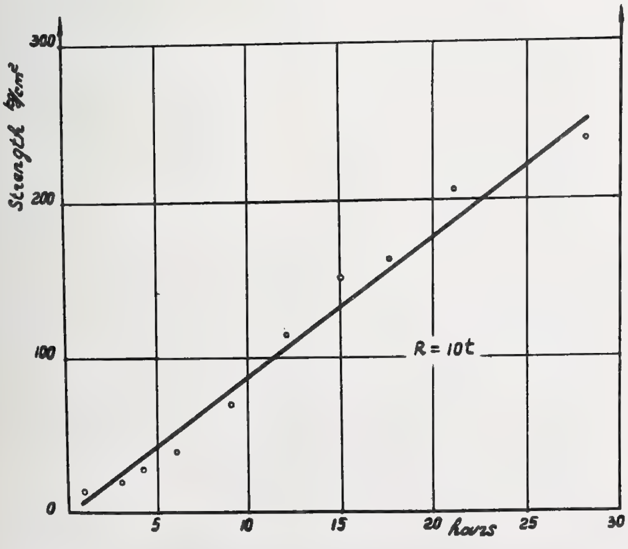

FIGURE 13. *Strength increase of SC mortar isolated in paraffin.*

Essentially the linear law of strength increase is maintained, being expressed by the equation: $R=10t$; the strength required to be attained during isolated hardening, about 200 kg/cm², is reached after 24 hr.

The selected SC components passed systematic and prolonged checking in pastes and 1:1 mortars, to establish the time stability of their mechanical properties.

Investigations were carried out on expansion, water absorption, strength in "free" and restrained conditions, self-stressing value in relation to degree of reinforcement (average for possible use, 1 percent), and other properties.

For selecting the required quantity of high-alumina cement with 14 percent gypsum, many combinations were investigated, by varying high-alumina cement content from 4 to 32 percent.

Results of 28-day investigation of SC mortar are shown in figure 14. Optimal high-alumina cement admixture of 18–20 percent gives the highest strength, 650 kg/cm²; highest expansion, 2.1 percent; and maximum water absorption, 6 percent (by weight).

Investigation of SC mortar properties with respect to time is shown in figure 15. Here during 6-hr heating: strength of "free" specimens increased from 160 kg/cm² to 268 kg/cm², and strength of restrained specimens increased to 310 kg/cm²; expansion and water absorption were low, 0.20 percent and 0.5 percent, respectively; self-stressing equalled 16 kg/cm². In further water storage, at 28 days the strength was 420 kg/cm² for "free" specimens and 450 kg/cm² for

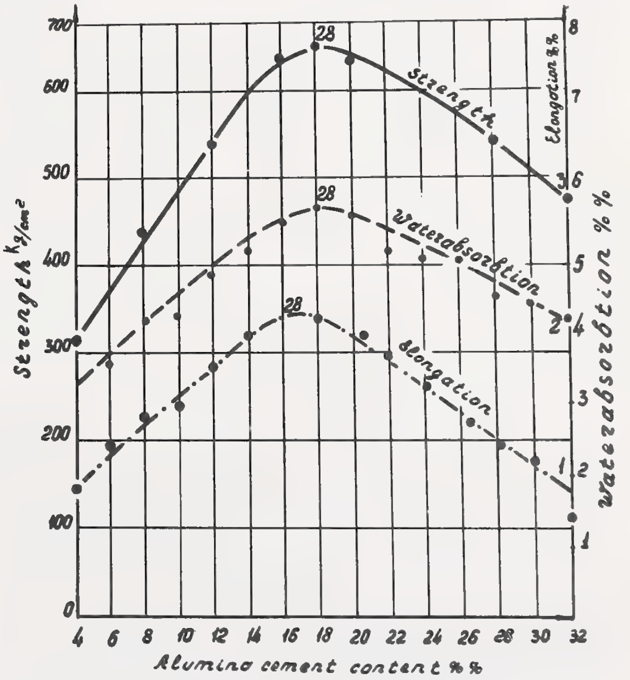

FIGURE 14. *Elongation, strength, and water absorption of SC mortar (1:1) with 14 percent gypsum, versus alumina cement content.*

Heated at 100 °C for 6 hr.

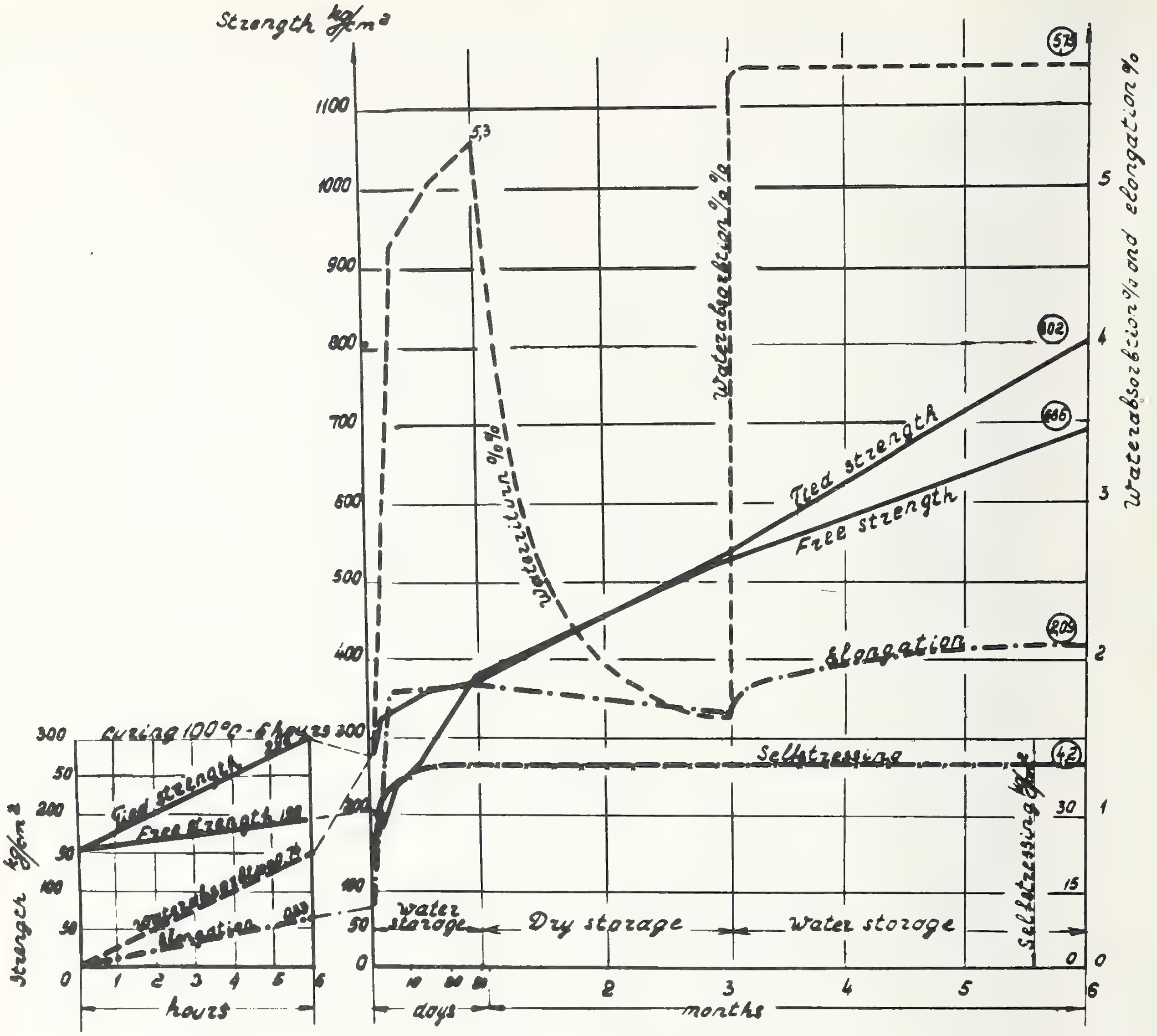

FIGURE 15a. *Elongation, strength, and water absorption of self-stressing SC mortar (1:1), versus storage condition (water-air).*

Proportions 14:20:66.

Heated at 100 °C for 6 hr.

restrained specimens; expansion was stabilized at 3 days (at 2.3 percent) with slight increase to 7 days; water absorption practically ended on the 14th day at 5.6 percent, and on the 28th day was 5.8 percent; self-stressing ended completely within 14 days and was 42 kg/cm².

After 6 months, the following results were obtained: strength of "free" specimens, 614 kg/cm²; restrained specimens, 740 kg/cm²; expansion, no change, i.e., 2.33 percent; water absorption, 6.7 percent; self-stressing, no change, i.e., 42 kg/cm².

It is important that during water storage the strength always continuously increases and reaches a high value, approaching 1,000 kg/cm² in 2–3 yr. We were more interested in the strength of restrained SC samples, as this is the chief characteristic limiting the relatively small deformations of reinforced self-stressed mortar.

At present, data are available on stable strength and the degree of self-stressing of SC mortar samples stored in water for 6 yr, this showing conclusively that all expansion processes are over, after the first several days of mortar existence.

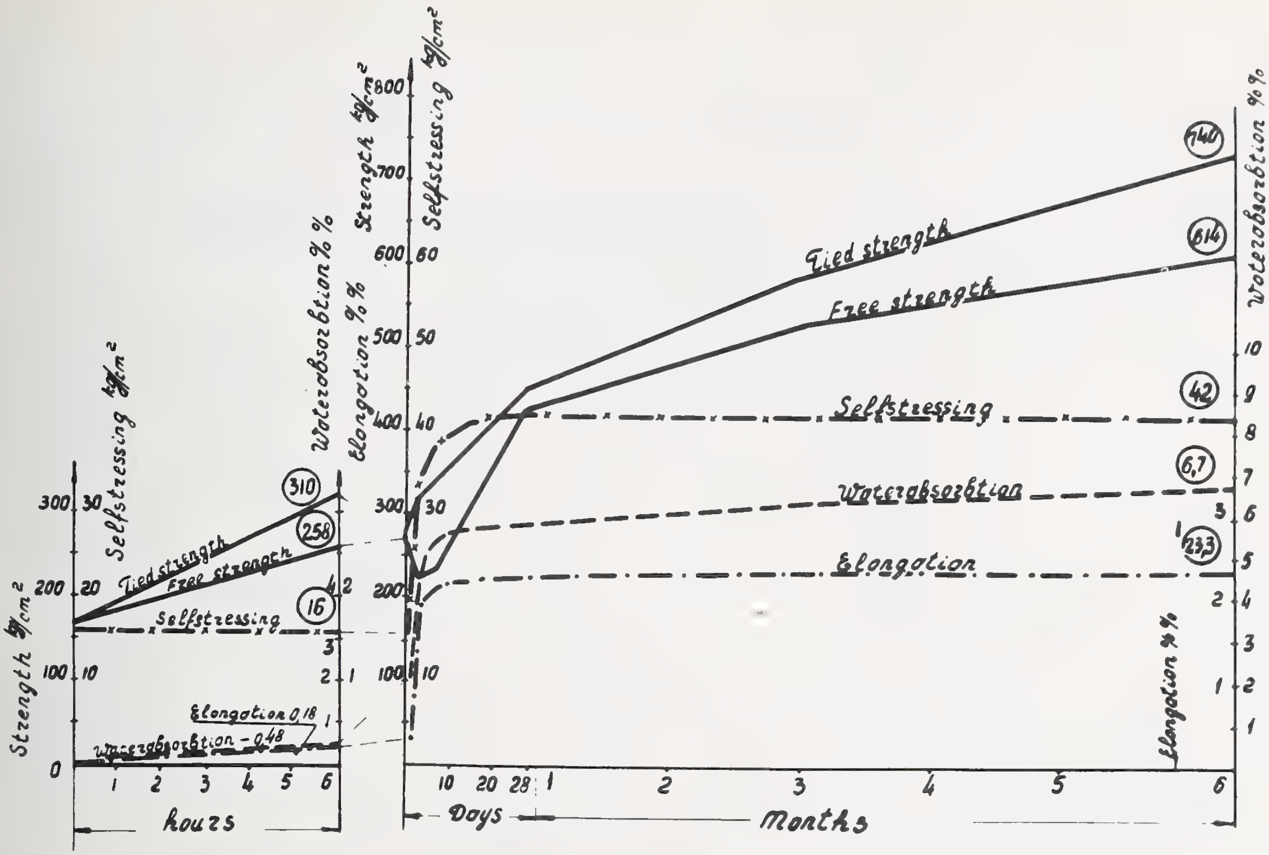

FIGURE 15b. *Elongation, strength, and water absorption of self-stressing SC mortar (1:1).*

Proportions 14:20:66.

Heated at 100 °C for 6 hr.

Water Absorption and Water Loss of SC Mortar. Influence of Initial Water-Cement Ratio. Influence on Self-Stressing of Premature Destruction of Initial Structure During Formative Period. "Stress Calibration"

Water absorption of SC mortars is of some interest. Water absorption is sufficiently high—for some combinations, 7–8 percent. Naturally, not all water is used for $C_3A(C\bar{S})_3H_{32}$, C_4AH_{13}, and other formations. Apparently up to 70 percent of this water should be considered as hygroscopic moisture. However, it is very characteristic that, during drying, this water leaves the system slowly, but is absorbed again very quickly. Apparently, the capillaries in the structure are widely branched and very fine, this explaining the complete impermeability of SC mortar. SC mortar samples 25 mm thick resist hydrostatic pressure of about 20–25 atm without any signs of sweating.

Absorption and water loss properties are clearly shown in figure 15 for SC mortar (1:1); cement composition 14:20:66 with hydrothermic treatment at 100 °C for 6 hr. Strength of restrained specimens is 802 kg/cm² after 6 months.

Mortar specimens absorb 5.3 percent water in 28 days. Removed from water and exposed to natural drying conditions for 2 months they lost 3.5 percent of the absorbed water and retained only 1.8 percent. Again immersed they reabsorbed the lost amount of water. It should be noted besides that a large variation of the moisture content of SC mortar slightly changes specimen length. Thus, 1.8 percent expansion at 28 days is lowered, as a result of 2 months isolated storage, to 1.6 percent, i.e., by 0.2 percent. Further moist storage not only restores initial expansion, but exceeds it.

For combinations of optimum high-alumina cement content, water absorption is higher, some water remaining in the system no matter how long the specimens are stored in air.

Figure 16 shows data on water absorption and water loss of the 1:1 mortar for SC with 11 percent gypsum, and variable high-alumina cement content, 4–32 percent. Combinations containing 16, 18, 20, and 22 percent of the high-alumina cement absorb about 6.1 percent water and lose

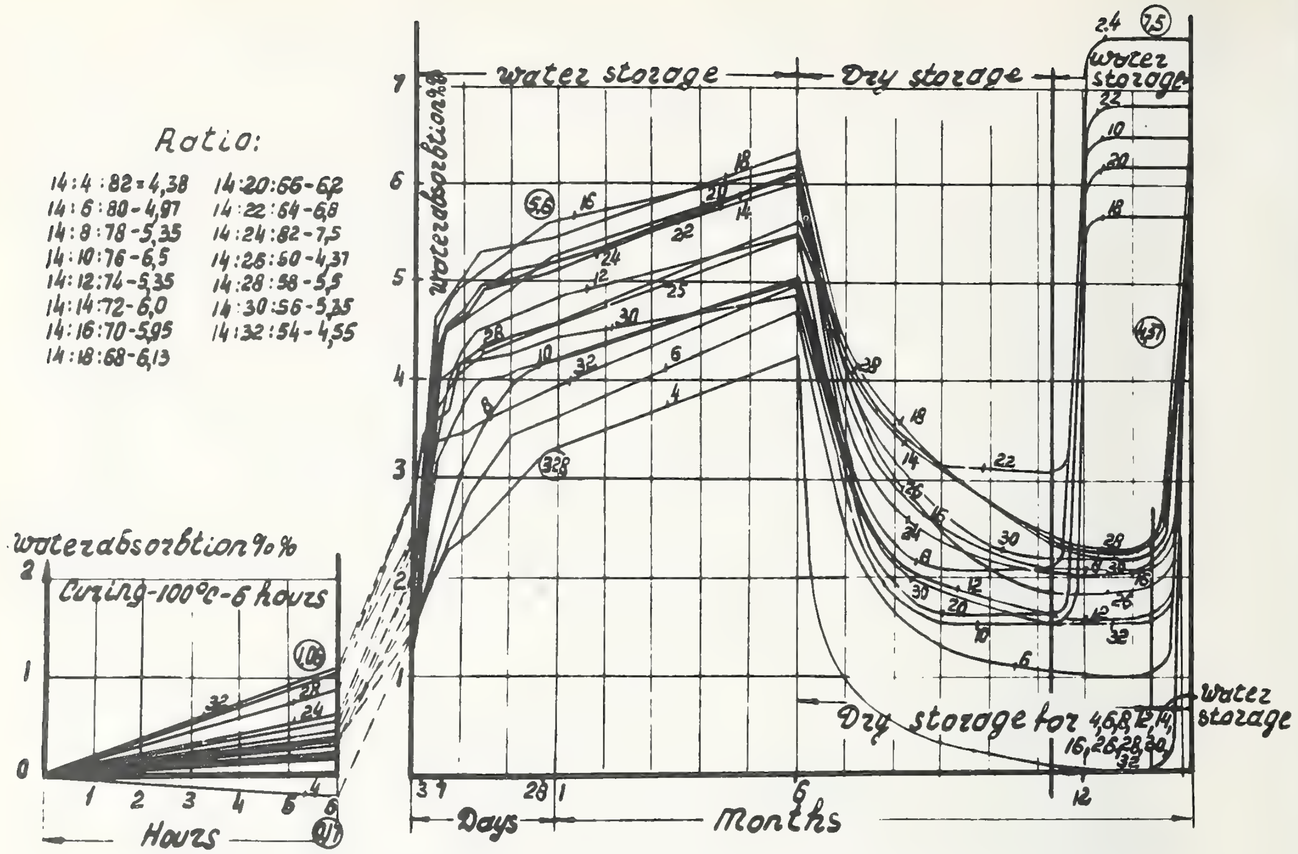

FIGURE 16. *Water absorption and water loss depending on storage condition (water-air-water).*

on the average 3.5 percent, retaining 2.6 percent. Combinations with 4 percent, i.e., almost without any high-alumina cement, absorb 4.2 percent and lose the same amount. As noted above, water loss during 6 and even 8 months is slow, while absorption is rapid.

Of some importance is the influence of the degree of repeated drying and absorption on self-stressing value. Does self-stressing disappear completely after some time? For determining this, expansive power measurements (fig. 17) have been made on 5 series of specimens differing only in hydrothermal treatment period: 1, 2, 3, 4, and 6 hr (see graphs from top to bottom). The sequence for all samples: water—20 days; air—15 days; water—20 days; air—20 days; water—25 days; air—35 days.

The investigations have shown that during drying about half of the initial self-stressing value is lost. Repeated moistening restores almost the entire self-stressing value. During these investigations it was determined that samples heated 6 hr lose practically nothing, i.e., during moistening they completely restore the initial self-stressing. The samples heated 2 hr irrevocably lose up to 15 percent of the initial self-stressing after several drying and moistening cycles.

Consequently, 6-hr hydrothermic treatment has several advantages over 2-hr treatment and it should be recommended for production of self-stressed structures.

Figure 18 shows investigations of strength and expansion of 1:1 mortar made with SC proportioned 14:12:74. In one case it received normal hydrothermic treatment at 100 °C for 6 hr and then water storage, in another case it underwent natural hardening in the paraffin-isolated condition. The specimens hardened in paraffin isolation for 14 months.

The mortar (1:1) that received normal hydrothermic treatment reached after 14 months of water storage a strength of 900 kg/cm^2, and expanded 1.9 percent at 10 days. Isolated dry-stored mortar had a very low strength—155 kg/cm^2; apparently, the calcium hydrates and hydrosulfoaluminates during formation and partial recrystallization absorbed the entire mixing water reserve (30 percent); there was not enough water for C_3S and C_2S hardening, and hydration stopped. In this case, specimen expansion was 3 percent, thus higher than for the first group. When, after 14 months, samples were immersed, water absorption was so rapid and the forces caused by calcium hydrosulfoaluminate recrystallization so large that the samples were rapidly and completely demolished.

The behavior of SC mortar specimens that had received hydrothermic treatment shows that SC

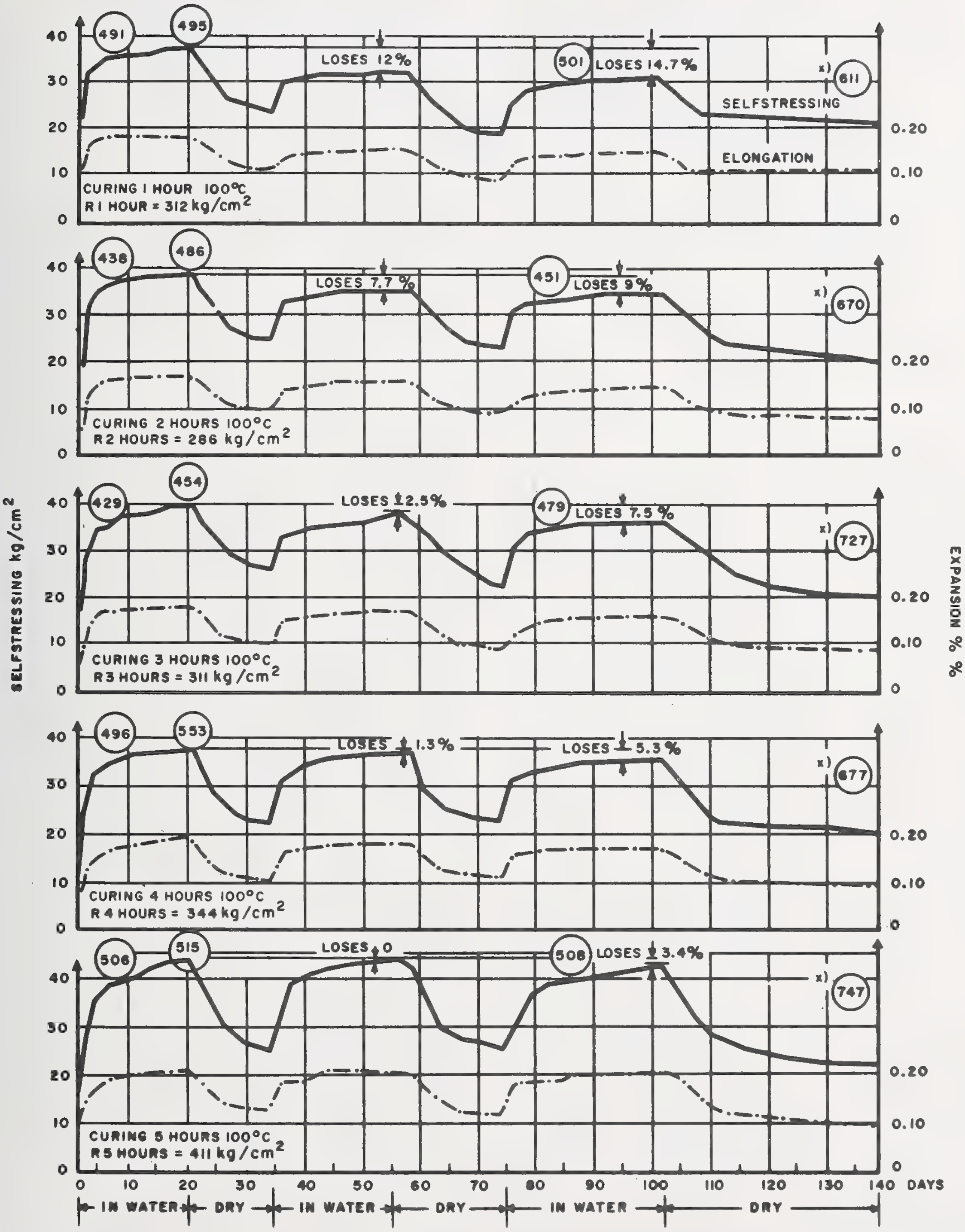

FIGURE 17. *Wetting and drying condition of self-stressing SC mortar (1:1).*

Proportions 14:20:66.

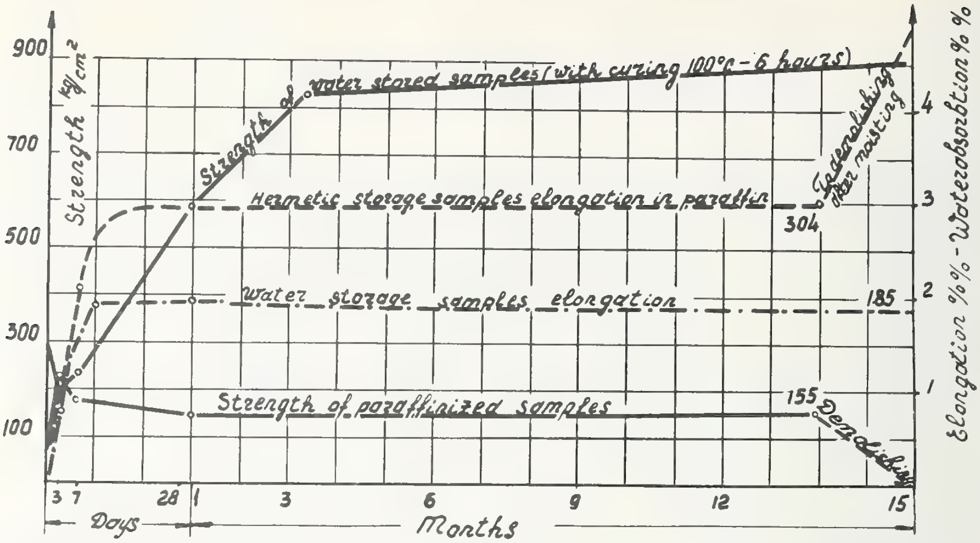

FIGURE 18. *Influence of water storage on elongation and strength of SC mortar (1:1) after heating at 100 °C for 6 hr in comparison with paraffin-isolated SC mortar (1:1) hydrated without heating.*

Proportions 14:12:74.

is a full-value hydraulic cement because of its hydrothermic treatment and its maximum strength reached during long-term moist storage. Therefore it should be employed for structures under pressure, in pressure pipes, tanks, in underground structures, and in highly moist conditions.

During investigations of SC mortars (1:1) it was found that the lower the water-cement ratio, the higher the self-stressing and strength. Very short SC mortar setting period, 2 min, hampered mortar batching and placing in molds. Vibratory mixing and vibratory casting, and cement retarding agents like lignosulfonates, were therefore necessary (½ percent sulfate-alcohol waste additive or tartaric acid, ⅒ percent technical). These setting-retarding methods are effective, but in both cases the degree of expansion is lowered and self-stressing is about 30 percent less. This is caused by the fact that in both cases there is destruction of the initial, rather friable, but very convenient frame structure of self-stressed SC, owing to which the frame structure, an essential part in expansion, is without strength in the spaces free of cement glue.

The self-stressing of 1:1 stressing mortar makes it possible to obtain an average concrete self-compression value in the range 20 to 50 kg/cm². This self-compression is the result of the structural reinforcement's elastic resistance to expansion, there being stressing to different degree, depending on reinforcement dimensions, over the range of 14,000 kg/cm² to 3,000 kg/cm², for 0.15 to 1.5 percent of reinforcement. For many structures such a prestressing value gives a satisfactory effect. With reinforcement higher than 1.5 percent, the concrete self-stressing intensity remains almost unchanged. However, the self-stressing value in the member sections may be changed as a result of a technological action, which we call "stress calibration". By special methods of stress application, both before and after hydrothermic treatment, it is possible to redistribute reaction forces in a member to any limit, and then the degree of fiber stresses in concrete may reach at least 150 kg/cm².

It should be noted that investigations have been made in the USSR in the coal mining industry when designing structures for reinforced concrete mine propping. The main requirements for propping members are low weight and high load capacity (about 10 tons/m²). During investigation of self-stressed vibrated bracings (channel type) with 0.75 percent reinforcing of the bracing section and 1.8 percent in the bracing tensile zone reinforced with high strength wires, the following stressed bracing conditions were obtained, by hydrothermic treatment for 6 hr at 100 °C and then 3 days water storage. High (6,000 kg/cm²) stresses in the upper reinforcement and comparatively low (1,500 kg/cm²) stresses in the lower reinforcement resulted in uniform compression of the concrete bracing, intensity 22 kg/cm².

The "stress calibration" [16] employed for bracings at stresses of 8,200 kg/cm² of the lower reinforcement made it possible to redistribute the stresses. Then the lower reinforcement in the middle part of bracings received a stress of 6,900 kg/cm² and the upper a stress of 800 kg/cm². The diagram of concrete stress distribution of the bracing section now shows the following fiber stresses: at bottom 200 kg/cm² and at top −47 kg/cm² (tensile). The method of "stress calibration" is still new and practical application will be possible, after much testing.

All above-mentioned SC mortar investigations refer to vibration during mixing and placing, owing to which the average self-stressing value obtained—40 kg/cm²—is lower than the actual

SC mortar self-stressing value, about 60 kg/cm², not yet reached for vibrated samples. The actual self-stressing values, corresponding to the SC chemical possibilities, were obtained with SC mortar by shotcreting. The dry mixture, delivered from the cement gun by compressed air at a pressure of 3–5 atm through a hose to the nozzle, was moistened at that point by water under pressure, and then thrown with high speed against the surface of the cast article. From the moment of moistening to placement by the gun, only hundredths of a second passed. Therefore, mortar placed by shotcreting is very dense, with minimum water content (about 0.20–0.22) and it is placed long before SC setting begins.

The advantages obtained by shotcreting technology can be enumerated: self-stressing reaches 50–60 kg/cm², and the strength at mature age is 80–1,000 kg/cm².

Self-Stressing of SC Pressure Pipes. Production Technology of Pressure Pipes and Their Testing

In the USSR the technology and equipment are simultaneously being worked out for three methods of manufacturing self-stressed pipes: shotcreting, centrifuging, and vibrosqueezing. Each of these methods provides for manufacture of pipe of specific diameters: shotcreting for pipes of dia. 600 to 1,000 mm, centrifuging for pipes of dia. 300 to 500 mm, vibrating-squeezing for pipes of dia. 150 to 250 mm.

The pipes manufactured by these technological methods retain internal pressure, without sweating, up to 15–20 atm, and may be used for operations under working pressures of 6 and 10 atm.

A special two-seat automatic machine (fig. 19) has been designed for making pipe by shotcreting. The automatic machine is equipped with a slowly rotating core (4), with foldable mechanism to make clearance between the shotcreted pipe and core. Besides, the machine has a rotating coil and wire reel (8), which may either be held by an electromagnet (7) and moved up and down with a platform (3), winding wire around the pipe, or may turn together with the core, remaining in the bottom no-work position (as shown in fig. 19). A set of nozzles is installed through which the SC mortar is shotcreted on the core to form the pipe. While the pipe is being manufactured in one station (LH), the other (RH) is used for preparatory operations. During rotation of core and motion of the platform (3) up and down, shotcreted layers are placed at the same time as the reinforcement coils. When the last layer is being placed, the surface is smoothed with a mechanical knife. After the first pipe casting (in the LH station), the set of nozzles is turned 180° and shotcretes the next pipe (in the other station), and so on. In the first station, the core is retracted and the pipe is removed by lifting it onto a round support and is transferred for further technological treatment, while the core is prepared for new shotcreting.

Figure 20 shows the technology worked out for self-stressed pipe manufacture. The shotcreted pipe, already hardened due to the quick setting of SC, is lowered for 1 min into a pit filled with melted paraffin to make a thin isolation layer, and is then stored for 18–24 hr at normal temperature, which gives the pipe a concrete strength of 200 kg/cm². Then the pipe is placed for 6 hr in boiling water, and into a cold water tank for 5–6 days storage. Finished pipe receives face leveling and hydraulic testing, and is transfered to the warehouse, where it is kept for 21–28 days.

The centrifugal technology of self-stressed pressure pipes has been checked at a Moscow pipe factory. Self-stressed pipes of 400-mm diameter, 50-mm walls, and 4 m long are manufactured there, whereas open channel pipes were previously made in solid molds using paraffin. Difficulties of the short setting time of SC were eliminated by use of a mixer equipped with a vibrating device. Ten min vibromixing destroyed the initial structure to a degree, so that the mixture retained plastic consistency for 30 min, sufficient for centrifuge casting. Pipe manufactured in this way with reinforced frame of stressing mortar was held in paraffin coating 24 hr during which the concrete strength reached 160 kg/cm². The pipe was next heated in a bath 6 hr at 100 °C, and then delivered for water storage. Internal pressure testing of these pipes showed that pipes with weak reinforcement resist internal pressure to 11–12 atm. Wound with prestressed design spiral reinforcement the pipe resists 25–28 atm pressure without leakage. Pipes without stressed coils can be used for pressure piping under 6 atm pressure, with winding for piping water at heads of 10 atm and above.

The technology of pressure pipe vibrocasting of small diameter pipe—150–200 mm, 2 m long, and with 25–30-mm walls—has been mastered on a vertical vibrosqueezed pipe casting machine, now industrially used (fig. 21). These pipes are equipped with spigots and are for use in water distribution lines and in pipings for water supply in rural areas with a working head of 4–6 atm. The pipes have cold-drawn wire reinforcement, diameter 4–5 mm.

The vibrosqueezing method of manufacture consists of a vertical vibrating mold slowly filled from the top with SC mortar mixture. A simultaneously vibrating core, introduced from the mold bottom, moves up and down rotating from one side to the other repeatedly, and distributes and tamps the mortar into pipe body and spigot. The simultaneous vibration of core and mold aids in compacting stiff mortar and in casting pipe. When the vibrating core is removed from the mold

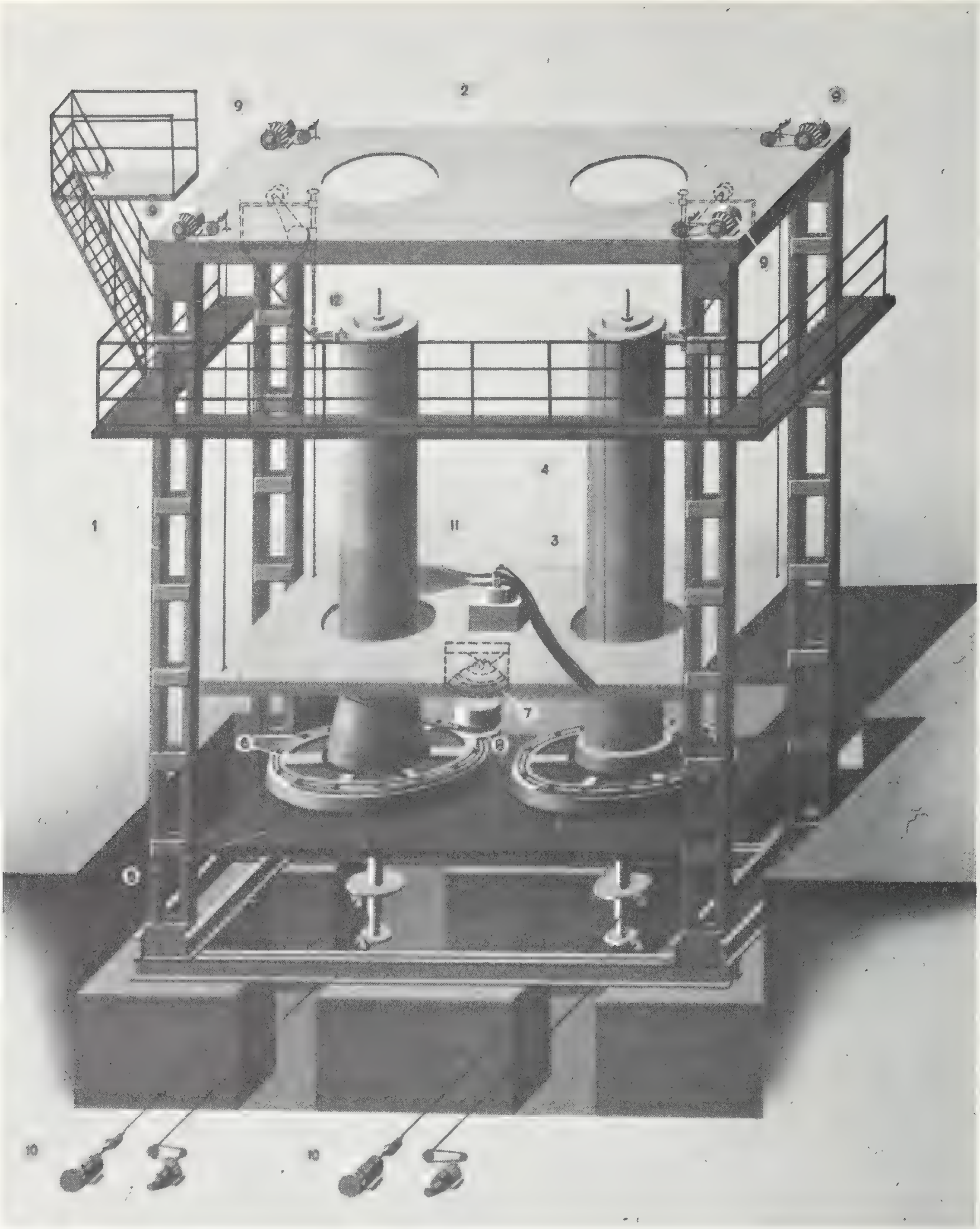

FIGURE 19. *Scheme of industrial automatic shotcreting machine for large-diameter, high-pressure pipe production.*

1. Stand
2. Upper platform
3. Movable platform
4. Collapsible metal core
5. Lower platform
6. Revolving table
7. Magnetic chuck (or clutch)
8. Spool with wire
9. Elevating motor
10. Motor for rotating table
11. Nozzles
12. End-forming device

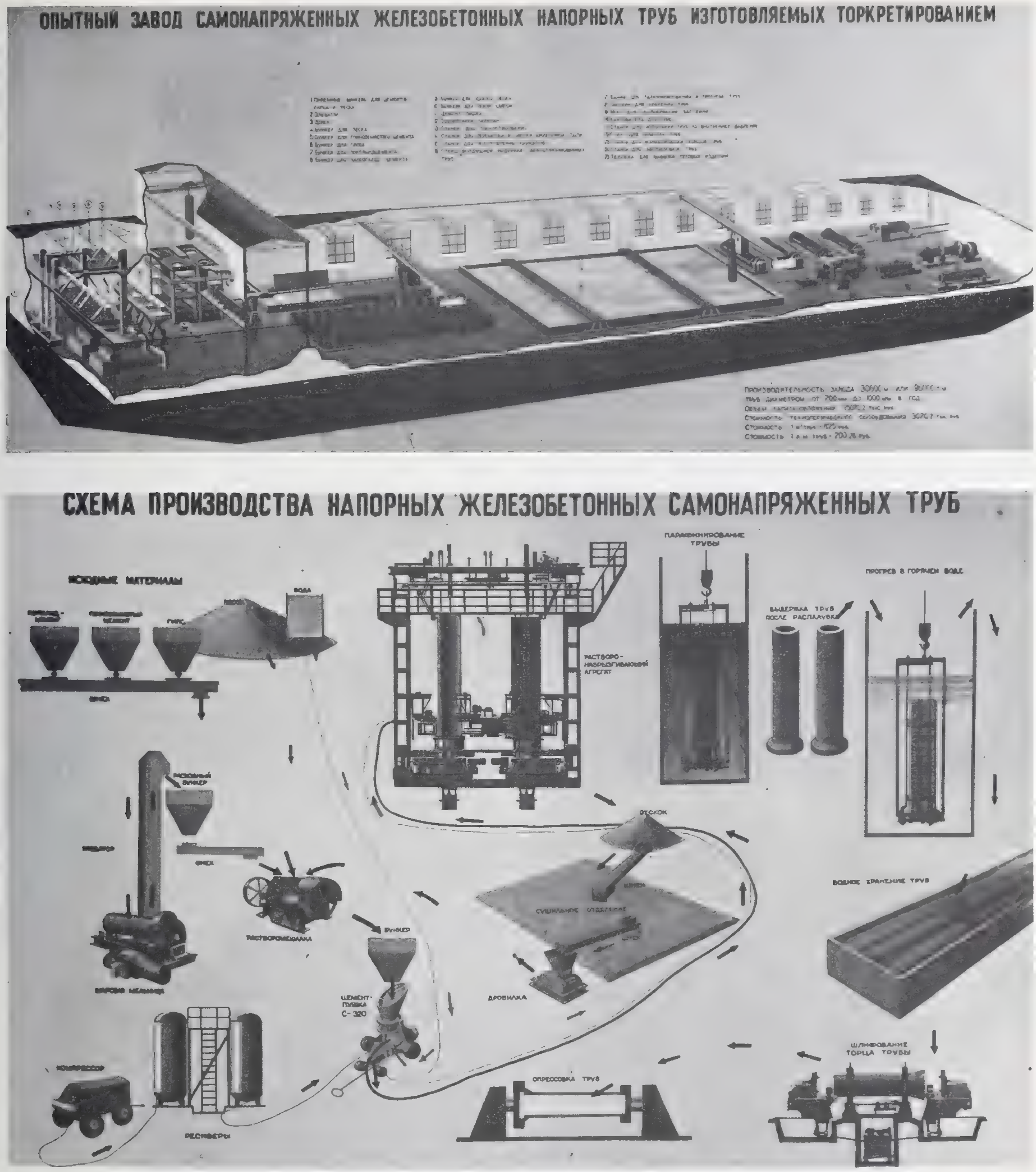

FIGURE 20. *Technology sequence of high-pressure pipe production by shotcreting.*

at the top end it pushes out excess mortar (if there is any) from the pipe. At this time vibration is switched off, and the core, while turning toward one and the other side, is pushed down, sliding along the internal pipe surface and smoothing it. The machine simultaneously casts two pipes over two cores. After the pipe casting process is finished, the molds are removed from the machine and are stored 12–18 hr, during which the concrete reaches a strength of 200 kg/cm^2. Then delivered pipes are heated 6 hr in a bath at 100 °C, when the pipe mortar reaches a strength of about 300 kg/cm^2. During subsequent water storage for 3–5 days, the mortar expands and pipe concrete and reinforcement are self-stressed. Here, as well as when centrifuging, vibrated mixing of the mortar occurs before and during the filling of the molds, due to which a significant part of the self-stressing is lost.

Testing of such pipes by internal pressure has shown that they have high impermeability. Even though 20–25 mm thickness of the wall is small, the pipes resist an internal pressure of 17 and even 25 atm without sweating.

A similar sequence is employed for manufacturing and testing pressure pipes by shotcrete casting. A horizontal spraying machine is used for shotcrete casting (fig. 22). In 1958 this machine was redesigned and is now equipped with mechanism for winding spiral reinforcement at the same time as shotcreting. It must be pointed out that previously whenever frame reinforcement was put on the shotcreting process had to be stopped, and it was necessary to remove the pipe with the core from the machine, to tighten the next reinforcement frame, and then to reinstall the pipe on the machine for further shotcreting. If the pipe had more than two reinforcement frames, shotcreting had to be stopped twice. This complicated the casting process and worsened the

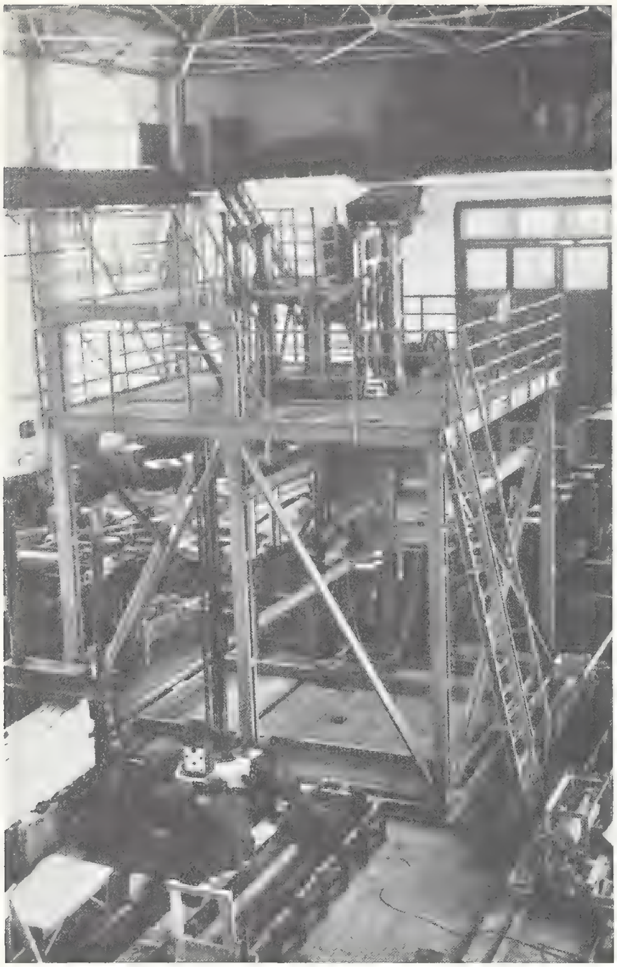

FIGURE 21. *Research vibrosqueezing machine for small-diameter, high-pressure pipe production.*

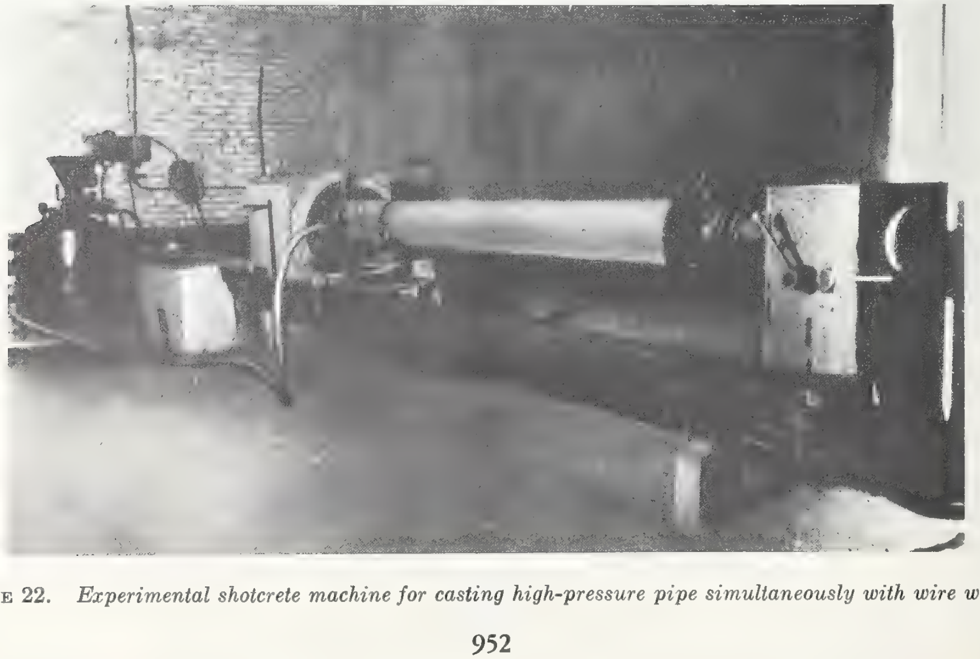

FIGURE 22. *Experimental shotcrete machine for casting high-pressure pipe simultaneously with wire winding.*

density of mortar under the spiral frame. Simultaneous winding of spiral reinforcement during the shotcreting process results in marked lowering in casting time, permits winding many rows with a wide pitch, reliably coats mortar around spiral wire, and may eliminate the need for longitudinal reinforcement.

As a result of shotcrete casting, with simultaneous entire pipe-body winding (throughout the entire wall depth) the spiral reinforcement with interwinding coils of adjacent rows is distributed uniformly in the concrete. In this condition mortar deformations during expansion are slight, thus insuring better use of mortar expansive power and corresponding maximum pipe self-stressing. During the mastery of new type shotcrete casting, it was found that simultaneous winding is the best method of reinforcing self-stressed pipes. Shotcreting needs a nonretarding admixture. Under these conditions the structure formed cannot later be destroyed. Due to the very low water-cement ratio, 0.16–0.22, the maximum quantity of "low-sulfate" hydrosulfoaluminate of calcium is formed and, consequently, maximum power is released for expansion and self-stressing during recrystallization into the "high-sulfate" form. This has been entirely verified by tests. In all cases shotcrete mortar specimens had high expansive force, and produced mortar self-stress of about 40–50 kg/cm^2. These results permit us to consider shotcrete casting as the chief method for manufacture of large diameter pressure pipes. Self-stressed shotcrete concrete has high stability in aggressive media, sea water in particular.

Conclusion

The idea of self-stressed structures, on which many Soviet scientists have worked (Mikhailov, Popov, Litver, Berdichevsky, Karasiev, and Potashnikov) is new in the field of prestressed reinforced concrete. The present level of development of the self-stressing method is progressive in character and has wide perspective for construction use, but also indicates need for further study to improve cement composition and retarding admixture for setting, and need for investigation of more effective self-stressing methods, including water hydration without heating and the method of "stress calibration," in order that one may progress from mortars to concrete with less binding material.

In the USSR, besides the explanation of self-stressing already discussed, G. N. Sivertzev holds another opinion, completely denying the possibility of calcium hydrosulfoaluminate formation in cement media and giving a different explanation for causes of expansion and self-stressing. Sivertzev considers that expansion may develop independently of formation or lack of calcium hydrosulfoaluminate, and that the contradictory phenomena occasionally observed during SC hardening are explained only by colloidal chemistry. Expansion is considered by him to be determined by the unstable dynamic equilibrium of two mutually contradictory processes, namely SC setting and hardening, and solvation processes of SC particles retarding coagulation. SC is marked by the presence of certain antagonistic suspensions (portland cement, high-alumina cement, gypsum, etc.). Here each type of solvate shell of the particles is formed separately, without disorientation of water dipoles, preventing adhering of particles. As the solvate shells cause cement paste expansion, the structure densifies and strength increases. Solvation and expansion develop with unavoidable structure friability and strength drop. During the hydration of ordinary nonexpansive cements, in dense pastes, the solvate shells invariably interfere, causing disorientation of the water dipoles and solvate shells. The solvate shells in this case lose their stable function and aid the direct cohesion of hardened cement paste particles. Sivertzev is conducting very interesting investigations to corroborate and broaden his veiws on SC expansion and self-stressing processes.

In France much work in the field of expansive cement has been done by the French scientist H. Lossier [18], who has produced his own expansive cement. This cement is composed of portland cement, sulfoaluminate cement, and slag, dry-ground in the proper proportions. Fifteen-day hardening in moist condition causes complete expansion and densifies the structure. According to Lossier, resistance should give self-stressing.

The theoretical conclusions of Lossier clearly show the established order and views on cement, and also show that scientists experimenting in this field must find the best mineralogical cement composition, the necessary additives, and the appropriate water content. The view is that the structural synthesis during cement setting and hardening takes place by itself, and forms the cement paste of required characteristics. This is beyond human influence. At best, the required structural formation processes may be accelerated by normal heating or high pressure. This considerably handicaps the designer, when it comes to the mixed cement passing through the required stages (fig. 7) of structural formation and strengthening.

P. S. Rehbinder and N. V. Mikhailov proposed intervention in the processes during the first stage. When preparing very fine cement, ground sand, and active mixture they recommend the use of mechanical influence like vibratory mixing of concrete and multifrequency vibration in all technological stages of mixture processing. This destroys the formed structure, to obtain denser packing of concrete and cement paste particles and development of hydration processes deeper in the cement grains. As a result there is a significant increase of concrete strength and density.

Our aims are broader: we prepare a binder so that the stage of structure formation passes quickly and setting is also rapid. We assume that the cement structure has entered far into the setting stage to form a sufficiently strong and hard cement paste body. With any absorption of water into this structure, even though it is very strong, expansion of cement paste completely destroys the structure, turning it into a jellified substance. Thus, the created structure conceals possibilities of self-demolition. In this respect SC is completely useless as a binding agent. But here the researcher intervenes in cement paste structure building and by definite processes (moistening, heating, mechanical force) rearranges the system, destroying certain cement paste structures, while others arise rapidly in the combinations and sequence required for the hard body to remain unchanged, so that strength is maintained and even increased, while the cement paste volume increases, able in case of resistance to convert deformation power into the work of reinforced concrete stressing.

Thus, cement acquires new qualities, previously not only not used, but even objectionable and in every way undesirable.

The possibility to direct the expansion of hardening binders, and freely to design them, is a new advanced undertaking in cement chemistry, opening wide technical horizons.

The work performed by Soviet scientists in this field is a first step towards using the chemical power of hardening binders, and must be continued in order to find the best way to release and make use of chemical forces inherent in the binders for advantageous work in self-stressing. The efforts of scientists and engineers of many countries should be directed towards this end. It seems to us that maximum results are assured if producers will participate in this work and introduce new achievements in their experimental plants.

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Discussion

Levi S. Brown

The advent and rapid development of prestressed concrete design and construction has opened a new field of broad application. Among the more intriguing variations is that of an expanding concrete member, essentially an expanding cement, whereby the desired prestress is self-effected. It is evident in the wealth of data presented in this paper that the concept, both of the cement and of its effective use, has developed into an established art. While the accomplishment merits high compliment, there are two or three facets of the report that may merit more extended discussion.

The unstable or expanding component of the cement (or concrete) is identified as low sulfoaluminate, proportioned about 35 to 65 percent portland cement. It is put into the cement as the two substances calcium aluminate and gypsum, properly proportioned. It is preserved in the low form by limited quantity of mix water. After thorough set, the hardened member is immersed in water. The availability of the extra water promotes alteration of the low sulfoaluminate to the high sulfoaluminate. The expansion is accomplished by this inversion. The expansion tends to disintegrate the formerly hardened member, which action of course is minimized by restricting the potential expansion, i.e., the low sulfoaluminate, to smaller proportions. If the expansion-curing is augmented and accelerated by heat, it is found that strength is maintained by autogenous healing. Thus a member may expand 3 percent or more, and the concrete still show a strength equal to or greater than that of the initial material. Test data, offered in some abundance, show this to be the eventual effect.

In practical application, a fixed principle of such expansion is that it is triaxial and that interior voids or discontinuities tend to increase in diameter. That is, the envelope of concrete about a prestressing wire tends to enlarge and thereby weaken bond and the desired composite action. Incidentally, elongation of the prestressing wire reduces its diameter and tends further to weaken the bond. This tendency is inherent in the process and should ever be kept in mind. That is to say, the adverse tendency does not necessarily vitiate the objective. It only means that one should be aware of corrective countermeasures. It may be that the autogenous healing automatically restores the bond. Then again, it is noted in the paper that uniaxial restraint tends to transverse compression, an explanation that is subject to serious challenge.

Many properties of the eventual concretes are investigated and described. Among others, a high resistance to sea water or sulfate exposure is noted. That probably is to be expected, since the aluminate is already in the stable high sulfate form. The concept offers intriguing possibilities in respect to endurance of ordinary concrete.

Nothing is said of one property that could be of wide interest. That is resistance to frost action. It is noted that before expansion the concrete is very dense and that it dries out very slowly. When put in water, however, it takes up water very rapidly. This anomalous behavior is quite different from that of conventional concrete. One may well suspect thereby that resistance to frost action could be poor, but no freezing and thawing tests were noted.

Much of the first part of the paper is made a dissertation on the processes of hydration and set of ordinary cement. While it is evident that intensive petrographic studies have been made, the concepts derived do not appear in full accord with conventional thought. For example, it is stated that the original cement particles shatter into much smaller colloids. Our petrographic studies do not support this view. Present purpose however is not to criticize the concept. It is only to note that the dissertation is not essential to discussion of the mechanism of expansion and self-stressing. The discussion suffers somewhat from this earlier and lengthy consideration.

Paper VIII–2. Blast-Furnace Slags and Slag Cements*

W. Kramer

Synopsis

The chemical process, temperature, and viscosity are important factors in the use of slag in blast furnaces. The MgO and Al_2O_3 content of the slag plays an essential role as well as the CaO/SiO_2 ratio. The chemical process and the physical state are decisive for the development of the hydraulic properties of granulated slag. The vitreous state of granulated slag is regulated by the temperature and viscosity of the molten slag and by the cooling conditions. Comparative tests of the action of the chemical composition of granulated slags on their hydraulic characteristics are possible only if the temperature of the melts prior to granulating is above the liquefying point.

Various investigations have revealed the interrelations existing between the tapping temperature, the CaO/SiO_2 ratio of the blast furnace slag, and its strength development under alkaline activation. They also have indicated the influence of a higher MgO or Al_2O_3 content on the hydraulic properties of the granulated slags. Contrary to MgO, a concentration of alumina will improve the reactivity of granulated slags. Cements made thereof, will, under alkaline as well as sulfate activation, experience an increase of strength. There are definite areas of preferred strength development under both activating methods. The interrelations between the hydraulic properties of blast furnace slags and the thermal equilibrium of paragenesis at the crystalline state offer a satisfactory assessing method for slags, the tapping temperature of which is higher than the melting temperature. However, in practical operation, this condition is not always fulfilled. For that reason, special attention should be paid to the glass content of granulated slag in addition to its chemical composition.

A method particularly suitable for practical operation because of its ease of application is the test under ultraviolet light. A quantitative analysis of the red colors of granulated slags is obtained by microscopic examination of fluorescence which, combined with the chemical data is a sufficient basis for assessing the hydraulic value.

The interrelations existing in the development of the technical properties of slag cements give evidence of the prevailing characteristics of the clinker in high-clinker types. In the low-clinker slag cements, the granulated slag is decisive for the hydration process and the strength development. For slag cements rich in granulated blast-furnace slag, the latent hydraulic setting power is released only by the alkalinity imparted to the fluid cement phase. The mineral structure of the clinker appears to be of influence on the strength development of this type of cement.

The processes occurring in the hydration of slag cements are dealt with in reference to the literature available. The possibility of forming links between different Si atoms by both oxygen and oxygen-hydrogen bridges, shown by H. O'Daniel, seems to merit particular attention in view of the importance for the stability of cements against attacking chemicals.

Résumé

La nature du procédé chimique, la température, et la viscosité sont des facteurs importants pour l'utilization du laitier dans le haut-fourneau. Comme le rapport CaO/SiO_2, la teneur du laitier en MgO et en Al_2O_3 joue un rôle important. La nature du procédé chimique et l'état physique sont décisifs pour le développement des propriétés hydrauliques du laitier granulé. La température et la viscosité du laitier fondu et les conditions de refroidissement ordonnent l'état vitreux du laitier granulé. Des essais comparatifs de l'influence de la composition chimique de laitiers granulés sur leurs propriétés hydrauliques ne sont possibles que lorsque la température des fontes avant la granulation est au-dessus du point de fusion.

Des différentes investigations ont découvert les relations qui existent entre la température de coulée, le rapport CaO/SiO_2 du laitier du haut-fourneau, et son développement de résistance sous l'activation alcaline. Elles ont montré aussi l'influence d'une teneur plus forte en MgO ou en Al_2O_3 sur les propriétés hydrauliques des laitiers granulés. Par contraste au MgO, une concentration de l'alumine améliorera la réactivité des laitiers granulés. Si l'on utilise ceux-ci pour la fabrication de ciments, on trouvera une accroissement de résistance sous l'activation alcaline et sulfatée. Des régions definies du développement de résistance maximale existent avec les deux méthodes activantes. Les rapports entre les propriétés hydrauliques des laitiers du haut-fourneau et l'équilibre thermique de la paragenèse à l'état cristalline offrent une méthode convenable d'évaluation des laitiers dont la température de coulée est au-dessus de la température de fusion. Néanmoins, cette condition n'est past toujours encontrée dans l'opération pratique. Ainsi, on doit faire attention spéciale à la teneur vitreuse du laitier granulé aussi bien qu'à sa composition chimique. A cause de son opération facile, une méthode particulièrement convenable à l'opération pratique est l'essai aux rayons ultra-violets. On obtient une analyse quantitative des couleurs rouges de laitiers granulés à l'aide d'une examination microscopique de fluorescence. Ceci donne, en combinaison aux données chimiques, une base suffisante pour l'estimation de la valeur hydraulique.

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Les relations qui existent dans le développement des propriétés techniques des ciments à laitier montrent à l'évidence les caractéristiques prédominantes du clinker dans les types de forte teneur en clinker. Dans les ciments à laitier de faible teneur en clinker, le laitier granulé est décisif pour le processus d'hydratation et le développement de résistance. Dans les ciments à laitier de forte teneus en laitier granulé du haut-fourneau, la tendance latente à prise hydraulique n'est libérée que par l'alcalinité conférée par la phase fluide du ciment. Il semble que la structure minéralogique du clinker influence le développement de résistance de ce type de ciment.

Les processus se présentants dans l'hydratation des ciments à laitier sont discutés en relation à la littérature disponible. La possibilité, montrée par H. O'Daniel, de former des liaisons entre différents atomes de Si pontés de liaisons d'atomes d'oxygène et d'atomes d'oxygène et d'hydrogène, semble à mériter l'attention spéciàle à cause de son importance pour la stabilité de ciments contre les composés chimiques agressifs.

Zusammenfassung

Chemismus, Temperatur und Viskosität sind die für die Schlackenführung im Hochofen bedeutsamen Faktoren. Der MgO- und Al_2O_3-Gehalt der Schlacken spielen hierbei neben dem CaO/SiO_2-Verhältnis eine bedeutsame Rolle. Für die Ausbildung der hydraulischen Eigenschaften der Hüttensande sind Chemismus und physikalischer Formzustand die bestimmenden Größen. Der glasige Formzustand der Hüttensande wird einerseits eingestellt durch die im Zeitpunkt der Granulation vorhandene Temperatur und Viskosität der Schlakkenschmelze und andererseits durch die Abkühlungsbedingungen.

Vergleichende Untersuchungen über den Einfluß der chemischen Zusammensetzung der Hüttensande auf ihr hydraulisches Verhalten sind nur dann durchführbar, wenn die Temperatur der Schmelzen vor ihrer Granulation über der Liquidustemperatur liegt. Die in der Berichtszeit durchgeführten Arbeiten haben die zwischen der Abstichtemperatur, dem CaO/SiO_2 Verhältnis der Hochofenschlacke und ihrer Festigkeitsausbildung bei alkalischer Anregung vorhandenen Gesetzmäßigkeiten dargelegt. Sie haben weiterhin den Einfluß höherer MgO- bzw. Al_2O_3-Gehalte auf die hydraulischen Eigenschaften der Sande aufgezeigt. Im Gegensatz zum MgO bewirkt eine Tonerdeanreicherung eine Verbesserung der Reaktionsfähigkeit der Hüttensande. Die aus derartigen Sanden hergestellten Zemente erfahren dadurch sowohl bei alkalischer als auch sulfatischer Anregung eine Anhebung der Festigkeiten. Für die Hüttenzemente bestehen bei den beiden Anregungsarten bestimmte Bereiche mit bevorzugter Festigkeitsausbildung. Die sich dabei ergebenden Zusammenhänge zwischen dem hydraulischen Verhalten der Hochofenschlacken und ihren thermischen Gleichgewichtsparagenesen im kristallinen Zustand geben bei Schlacken, deren Abstichtemperatur über der der Liquidustemperatur liegt, eine gute Beurteilungsmöglichkeit ab. In der Praxis ist diese Voraussetzung jedoch nicht immer erfüllt. Aus dem Grunde ist dem Glasgehalt der Hüttensande neben ihrem chemischen Aufbau besondere Beachtung zu schenken. Einen guten Aussagewert, der insbesondere wegen seiner Einfachheit und schnellen Durchführbarkeit für die Praxis besonders geeignet ist, besitzt die Prüfung im ultravioletten Licht. Bei Einsatz der Fluoreszenzmikroskopie lassen sich quantitative Aussagen über den "Rotgehalt" der Hüttensande als dem hydraulisch wirksamen Bestandteil machen, der zusammen mit den chemischen Daten des Hüttensandes eine gute Beurteilungsgrundlage für ihren hydraulischen Wert bildet.

Die in der Entwicklung der zementtechnischen Eigenschaften im Feld der Hüttenzemente vorhandenen Gesetzmäßigkeiten lassen den vorherrschenden Einfluß der Klinkerkomponente bei den klinkerreichen Hüttenzementen erkennen. Bei den klinkerarmen Hochofenzementen ist dagegen der Hüttensand die den Hydratationsablauf und die Festigkeitsentwicklung bestimmende Größe. Da bei den hüttensandreichen Hochofenzementen das latent hydraulische Erhärtungsvermögen erst durch die Alkalität, welche der Klinker der flüssigen Zementleimphase verleiht, ausgelöst wird, scheint der mineralische Aufbau der Klinker für die Entwicklung der Festigkeit dieser Zementart—insbesondere bei frühen Prüfterminen—von Einfluß zu sein.

Die sich bei der Hydratation der Hüttenzemente abspielenden Vorgänge werden abschließend anhand der vorliegenden Literatur behandelt. Die von H. O'Daniel aufgezeigte Möglichkeit der Brückenbildung zwischen einzelnen Si-Atomen sowohl über Sauerstoff- als auch über Sauerstoff/Wasserstoff-Brücken scheint im Hinblick auf ihre Bedeutung für die Beständigkeit der Zemente gegenüber chemisch angreifenden Stoffen besondere Beachtung zu verdienen.

Preface

At the Cement Chemistry Symposium held in 1952, F. Keil [1] [1] gave a comprehensive survey of the nature and value of the chemical characteristics and data as well as of the physical processes and technological methods elaborated for assessing the hydraulic properties of granulated blast-furnace slags. Since that time, literature on the subject of blast-furnace slags, their hydraulic properties, and the slag cements made thereof, has been enlarged by a series of research and test works.

The present report is intended to point out to what extent these works have helped to define and classify the manifold interrelations existing between the various factors that determine the different specific properties of granulated blast-furnace slags.

Test reports from the Soviet Union and the remaining Slavic-speaking countries could be taken into consideration only as far as translations or treatises contained in relevant trade journals, e.g., from the German Democratic Republic, have been available for evaluation.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The test results published prior to the Third Symposium will be referred to only at those points where it is found necessary for a better understanding of the recent works. The statements are completed by some provisional information on tests carried out by the Research Institute for Blast-Furnace Slags at Rheinhausen.

For some decades, blast-furnace slag has been of particular importance in the European countries for the manufacture of hydraulic binding agents. The specific properties this material imparts to the cements made thereof have led to an increased interest in its use as granulated slag in the manufacture of slag cements.

Influence of Blast-Furnace Slag on the Furnace Operation

In the blast-furnace process, the slag is deemed to play a purely metallurgical role. It will create the operating conditions required for obtaining a smooth working of the furnace and, at the same time, the quality of pig iron wanted. The interrelations taking place between the iron bath and the molten slag are regulated and determined by the chemical composition, the temperature, and the viscosity of the slag.

On the other hand, these factors are also of decisive importance for the development of the latent hydraulic properties of the blast-furnace slag as well as for the creation of the most favorable conditions for the conversion of the molten fluid into the vitreous state of granulated slag. Hence, a survey of the progress made and of the present situation in the field of slag cements should also take into account those works and researches dealing with the composing of slag in blast furnaces and the conditions of converting molten blast-furnace slag into granulated slag.

Among the great number of scientists studying, during the twenties and thirties, the natural laws of the blast furnace process with regard to the slag in connection with practical experience, C. H. Herty [2] and H. Schenck [3] should be mentioned first. By physico-chemical research, they contributed to an explanation of the processes taking place in the stack and the hearth of the blast furnace. In this way, the influence of slag regulation on the composition of the pig iron and the working of the furnace could be determined on a scientific basis. Experiments with the same or a similar purpose, considering some further factors of influence, have been carried out during the last 15 years by F. Koerber and W. Oelsen [4] as well as by W. Oelsen and other collaborators [5].

The investigations led to the finding that the development of both the pig iron and the slag in blast furnaces is the result of a long chain of consecutive, partly overlapping reactions. They set in shortly after the ore, coke, and fluxes are charged. Passing through intermediate reactions occurring in the shaft partly in the solid state, partly in the fluid stage, the process concludes by reactions taking place in the hearth between the metal melt and the slag bath. By properly selecting the composition of the slag and appropriately regulating the temperature, it is possible to influence the content of accompanying elements in the metal within broad limits to comply with the metallurgical requirements of the steel-making process, as well as to improve the quality of the slag products for conversion.

Without taking into account some special slags, lime and silica are the main components of blast-furnace slags as far as quantity is concerned. The *p*-value, i.e., the ratio of their oxides, constitutes one of the relative values which are used to characterize the blast-furnace slag by its chemical aspect.

Information on the reactions taking place between the CaO/SiO_2 basicity of the slag and the conditions of temperature and viscosity of the slags is given by the phase diagram of the three-component system $CaO–Al_2O_3–SiO_2$ by G. A. Rankin and F. E. Wright [6] as well as by the viscosity examinations of the four-component system $CaO–Al_2O_3–MgO–SiO_2$ by R. S. McCaffery and collaborators [7] which were recently completed by works of T. Saito and Y. Kawai [8] and further of J. S. Machin and T. B. Yee [9]. Changes of the CaO/SiO_2 ratio may therefore occur in acid slags within large ranges without strongly affecting the conditions of temperature and viscosity. However, for basic blast-furnace slags which are of particular interest for use as granulated material in the production of cements, a proportionate interdependence is given between these three values in conformity with the practical realities of blast-furnace operation. For basic ore and fluxes, the slag basicity and the hearth temperature, therefore, will be of decisive importance for the quality of pig iron produced. It is a general rule that an increase of the CaO/SiO_2 ratio will correspond to an increase of the content of C, Si, Mn, and P, and, at the same time, to a reduction of the content of S and N. As to slag cements, an increase of the slag basicity will generally result in a higher hydraulic value of the cements.

However, with basic slags, it will be possible only to a certain extent to raise the basicity by adding a larger quantity of lime to the fluxes. An increase of the lime content at unchanged conditions makes the slag quickly turn highly viscous. Trouble in the working of the furnace and changes of the reduction ratios can thereby only be avoided by substantially increasing the hearth temperature which will strongly affect the efficiency of the process.

The disadvantage of a higher lime content, however, may, to a certain extent, be eliminated by changes of the MgO and Al_2O_3 content of the slags.

An improvement of the flowing properties of high-CaO slags by adding larger amounts of MgO has been demonstrated by practical experiments on a large scale by A. J. Burgess and B. G. Baldwin [10]. The same fact was concluded from the results obtained by Soviet metallurgists such as J. P. Ssjemik [11]. An interesting and valuable survey of experiments at blast furnaces, particularly in the USSR, is presented by M. A. Pawlow [12].

A change of the Al_2O_3 content in blast-furnace slags causes an effect inverse to that of the CaO/SiO_2 ratio. Contrary to the CaO/SiO_2 ratio which, in acid blast-furnace slags, can be varied within a relatively far-reaching range without perceptibly affecting the temperature and the viscosity of the slag, changes of the Al_2O_3 content will be of considerable influence on the slags. The increased viscosity at a higher Al_2O_3 content will impede the use of high-aluminous blast-furnace slags for operating an acid furnace.

Yet, with basic blast-furnace slags, for which a small increase of the basicity results in higher melting temperatures and reduced viscosity, the metallurgical conditions of the furnace process will be improved by adding a larger quantity of alumina.

The favorable effect of such blast-furnace slags normally containing up to 20 percent of Al_2O_3 is known, according to O. Vorwerk and W. Kramer [13], for both the self-fluxing and the composed mixtures to which special alumina vehicles are added for regulating the alumina content. This feature was recently confirmed by F. Schrader [14]. He succeeded further in proving by practical experiments with Indian ores that an increase of the alumina content in slags up to 25 to 28 percent made the working conditions difficult in consequence of the resulting increase of viscosity. On a certain scale, a possibility of influencing the working of the furnace and the quality of the pig iron is offered by adding larger quantities of alumina to the blast-furnace slags.

As evidenced by the results of the investigations carried out by P. Huettemann [15] concerning the manufacture of basic steel and steel pig, it will be possible to convert a slag of high basicity without any reduction of efficiency only upon an increase of the Al_2O_3-content.

The above-explained effects of magnesia and alumina on the viscosity of blast-furnace slags refer to the circumstance of only one of the two components being variable. According to the studies made by E. F. Osborn, R. C. De Vries, K. H. Gee, and H. M. Kraner [16], this condition must be given, since the effects of magnesia and alumina on the viscosity of slags may not be summed up. To obtain an optimum viscosity by adding alumina, a normal MgO content of the slags will be required, whereas, on the other hand, the effect of an increased MgO content can be observed at a low Al_2O_3 content. The results of these research works have been confirmed by the above-treated operating experiments.

By way of laboratory tests, W. Oelsen, E. Schuermann, and S. Osman [17] investigated the effects of additions of alumina and magnesia in interaction with the iron melt and the slag bath. They came to an important finding for assessing the working of slag, viz, they found out that for calculating the basicity of a $CaO–MgO–Al_2O_3$–silicate slag, the value of MgO cannot be simply added to that of CaO, as the sulfur content of pig iron is largely determined by the CaO/SiO_2 ratio. With regard to desulfuring, the MgO must consequently not be rated as a complete lime substitute. For the same reason, alumina may not be looked upon as a lime substitute. It follows that the advantages of the MgO or Al_2O_3 content in basic slags lie in their effects of reducing the melting point or of improving the viscosity. Since alumina acts mainly as a liquefying agent in basic CaO slags, it would not be correct to add its value to the acids for calculating the basicity. In other words, the Al ion of basic melts may only be considered as a network-changing element at temperatures above the melting point. As known, the Al ion can act both as network-changing and network-forming agent. As blast-furnace slags should be granulated in such a way as to be largely frozen at the state of melting, the Al ion is maintained in such cases as a network-changing element of granulated slags.

The above studies should give rise to submitting the empirical formulae based on chemical analysis data to a critical examination. All measures referred to by the foregoing to contribute to improving the working of the furnace and the quality of pig iron will exert also a favorable influence on the hydraulic properties of granulated slags. The interrelations given between the chemical process, the temperature, and viscosity on the one side, and the hydraulic properties of the granulated slags on the other hand, have been explained by F. Keil by means of a survey of a series of former research works.

Operating Tests of Blast-Furnace Slags

Influence of Chemical Composition

For the last decade, large-scale practical tests have been carried out in blast furnaces, by which the effects of such measures on the quality of the pig iron, the working of the furnace, and the operating of the slag as well as on the hydraulic properties of the granulated slags produced were examined. O. Vorwerk and W. Kramer added as much aluminous iron vehicle (red mud) to high-basic ores and fluxes as proved necessary to obtain slags of a certain composition and of low viscosity.

The most favorable range of viscosity of these slags at relatively low furnace temperatures was deduced from the phase diagram of the three-component system $CaO–Al_2O_3–SiO_2$ given by G. A. Rankin and F. E. Wright and from the viscosity tests made on this system by R. S. McCaffery and collaborators. Simultaneously, these large-scale tests of practical blast-furnace operation confirmed partial results of the research done by E. F. Osborn, R. C. De Vries, K. H. Gee and H. M. Kraner on the optimum composition of blast furnace slag of the four-component system $CaO–MgO–Al_2O_3–SiO_2$.

The resulting slags were converted into slag cements after being granulated. The favorable action of increased alumina content on the hydraulic properties of basic granulated slags, either alkali- or sulfate-accelerated, could be proved in this way. The practical value of the tests is demonstrated by the evidence of a regulated slag composition leading by the resulting uniform and favorable working conditions to an improvement of the quality of the pig iron produced as well as of the blast-furnace slag.

P. Huettemann evaluated the operating results obtained in the manufacture of basic steel and steel pig with regard to both metallurgical and cement technical aspects. He succeeded in determining the essential values having influence on the reduction process and completed the study by an analysis based on a large number of operating data covering several years. According to his findings, the influence of increased alumina content on the strength development of cements is independent of the basicity of the slag, as far as the initial strength is concerned. For the strength obtained after a period of 28 days, however, such a dependence is evident. At low basicity, its effect will then be greater than at a high CaO/SiO_2 ratio.

Both these research works have promoted in Western Germany the manufacture of highly hydraulic granulated slags from slag solutions of composed ore and fluxes for the production of low-clinker blast-furnace and sulfate-slag cements exhibiting high initial and final strengths.

The dependence of the hydraulic properties of granulated slags on the slag composition and the furnace temperature was further thoroughly investigated by J. Roquejoffre [18]. The slag samples taken by him over an extended period, considering simultaneously the operating conditions, were examined with regard to their hydraulic characteristics. He found that among others there are interrelations between the tapping temperature and the CaO/SiO_2 ratio on the one hand, and between the CaO/SiO_2 ratio and the compressive strength on the other. Comparative tests of the hydraulic properties of four species of granulated and one species of crystalline blast-furnace slag were carried out by T. Tanaka and K. Takemoto [19] with the purpose of investigating the strength development of the cements made thereof by considering the chemical composition of the slags. A clear relation between the various characteristic values referred to for the hydraulic properties of granulated slags and the strength values of the cements made thereof could not be discovered. This lack of correlation is due to the fact that not only the properties of the slag melt will be of importance for the quality of a granulated blast-furnace slag, but also the conditions under which the slag is converted into the vitreous state.

Influence of Granulation

At an earlier date, G. Mussgnug [20] pointed out the influence exerted by the slag temperature on the development of the hydraulic properties of granulated blast-furnace slags.

By experimental examination of 150 slags derived from the blast-furnace tests carried out by A. J. Burgess and B. G. Baldwin, B. G. Baldwin [21] found that all slags could be completely converted into the vitreous state, if, prior to chilling, the temperature of the melt was some degrees above the liquefying point.

L. Blondiau [22] reported on the effects that substantial reduction of the temperature prior to granulating the slags will cause in the cements made thereof. He found out that, for example, a lowering of the granulation temperature from 1,538 to 1,479 °C will reduce the strength values of sulfate slag cements by 10 to 40 percent.

The influence of granulation is dealt with by W. Kramer [23]. Two species of granulated blast-furnace slags—produced from the same melt by different granulating conditions—were tested by him. The strength development of the cements made thereof differed, particularly among the low-clinker mixtures. The strength of cements made of granulated slag of low gravity and of foamed structure was 30 to 45 percent higher than that of cements made with slag of a compact vitreous structure. The influence of granulation was particularly great on the initial strength of the cements. By properly regulating the conditions of granulation, the hydraulic hardening of granulated blast furnace slags can be improved.

Test results of the influence of these cooling conditions on the hydraulic properties of hematite slags were reported by P. Bornatsch [24]. Three species of hematite slags of slightly varying chemical composition were subjected to different cooling conditions. The glass content of the resulting granulates was determined by microscope and brought in relation to the compressive strength of the slag cements made thereof.

By this method, the compressive strength could be determined from the glass content of the slags. Slight variations of the chemical composition of the slags tested were of no essential importance to the strength of the cement.

Examination of Synthetic Glass

For clarification of the influence exerted by the chemical composition on the development of the latent hydraulic properties of the granulated blast-furnace slags, a series of extended experimental examinations of laboratory slags and synthetic glasses have been carried out during the period under report.

E. F. Osborn, R. C. De Vries, and K. H. Gee determined the optimum composition of blast-furnace slags with regard to synthetic glass having a fixed alumina content, but varying amounts of CaO, MgO, and SiO_2.

Optimum compositions of slags were found to be as follows (percent by weight):

Al_2O_3	SiO_2	CaO	MgO
5.0	36.0	43.0	16.0
10.0	32.0	44.0	14.0
15.0	28.5	44.0	12.5
20.0	24.0	45.0	11.0
25.0	19.0	48.0	8.0
	(12.0) [a]	(57.0) [a]	(6.0) [a]
30.0	9.0	56.0	5.0
35.0	7.0	54.0	4.0

[a] The values in parentheses indicate a second optimum slag at the 25-percent level of the four-component system.

Further compositions closely ranging near the main points of the four-component system $CaO–MgO–Al_2O_3–SiO_2$ became completely fluid below 1,500 °C, and exhibited a maximum absorbing power for sulfur. The authors mention further that the optimum slag compositions will require a smaller amount of melting heat and will be of low viscosity. Slight variations of their chemical structure will, consequently, neither cause a sudden increase of viscosity, nor trouble the working of the furnace.

B. G. Baldwin examined the results of E. F. Osborn and collaborators by experimental tests of samples of blast-furnace slag he had taken from a working test (A. J. Burgess and B. G. Baldwin). The melting temperature and the viscosity conditions of about 150 slag samples were determined in a nitrogen atmosphere. An increase of the melting temperatures in consequence of the oxidation of FeO and MnO could thereby be avoided, but not the volatilization of part of the sulfur contained in the slags. It appears from the examination that the liquefying temperatures of blast-furnace slags deviate only slightly from the melting temperatures of the corresponding mixtures—based on the four oxides CaO, MgO, Al_2O_3, and SiO_2.

This relation was also found by E. E. Hofmann [25] by tests of blast-furnace slags under working conditions, by which the great variations of the results of measuring could be eliminated by the application of statistical analysis.

The diagrams published by E. F. Osborn and collaborators, therefore, are reliable for the determination of optimum compositions at 1,500 °C. Lower temperatures, due, e.g., to the operation of the furnace, or which could be caused by the material remaining too long in the ladle between tapping and granulating, will, at a constant Al_2O_3 content, lead to a separation of crystals and thereby to a lowering of the fluidity of the slag. The elimination of these effects which would be of disadvantage to the development of the hydraulic properties of granulated blast-furnace slags can be achieved via the chemical process by reducing the CaO content or increasing the SiO_2 and MgO contents of the slags.

The separation of crystals is connected with a change of the chemical composition of the melt. The resulting slag minerals, particularly the melilites and orthosilicates, are of greater basicity than the average composition of the remaining solution. This acid residual slag solution will not exert such favorable effects on the reactions wanted in the hearth of the blast furnace, as those obtained with the original slag after the latter has been converted into a homogeneous fluid solution by decomposition of the crystals. Such incorrect coordinations of slag composition and temperature leading to a separation of crystals, are of disadvantage to the quality of the pig iron produced as well as to the hydraulic properties of the granulated slag. These authors lay stress on the particular value of a regulated composition of the slag being in the interest of both the blast-furnace operator and the user of the blast-furnace slag.

F. Keil and F. W. Locher [26] manufactured more than 45 glasses of the three-component system $CaO–Al_2O_3–SiO_2$, of which about 15 glasses were melted with an addition of 5 percent of MgO. They examined the hydraulic setting properties caused by activation by means of clinker, anhydrite, and calcium hydroxide. The results of the strength tests were shown in the diagram of the three-component system.

In activating the glasses free from MgO by clinker, two ranges of high compressive strength could be observed, situated at 18 percent of SiO_2 and at 30 percent of SiO_2. The same glasses showed, however, only one range of high compressive strength, when activated by means of $CaSO_4$ and $Ca(OH)_2$, respectively.

The optimum strength of these glasses with any of the three activating agents was restricted to a small area of the three-component diagram and nearly concentrated to an approximate composition of 50 percent of CaO, 19 percent of Al_2O_3 and 31 percent of SiO_2.

An addition of 5 percent of MgO, making the glasses similar in composition to the blast-furnace slags produced in Europe, partly resulted in higher strength values under activation both by clinker and $CaSO_4$. The comparative strength development of four technical blast-furnace slags is quite in conformity with the results obtained with synthetic glasses.

The range of optimum compressive strength values of MgO-glasses under clinker activation, obtained after 28 days, is shown by figure 1 in the field of a 5-percent MgO content of the four-component system $CaO–MgO–Al_2O_3–SiO_2$.

When activating these glasses by means of $CaSO_4$, a narrow restricted area of high compressive strength will develop, approximately at

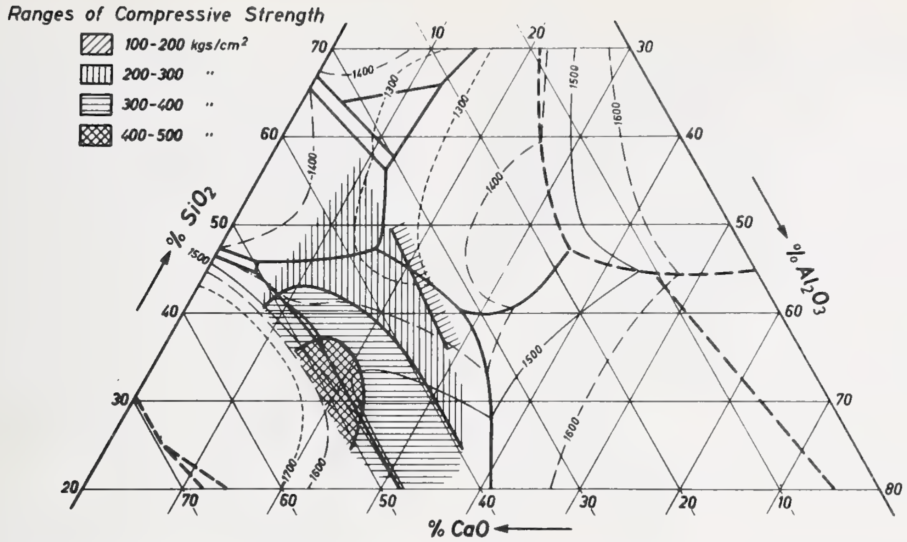


FIGURE 1. *Compressive-strength values, obtained after 28 days, of glasses of the* CaO—Al_2O_3—SiO_2—MgO *system stimulated by means of portland-cement clinker.*

Data referring to a 5-percent MgO level.
(According to Keil and Locher, 1958)

a glass composition of 48 percent of CaO, 5 percent of MgO, 18.5 percent of Al_2O_3 and 28.5 percent of SiO_2. When using $Ca(OH)_2$ for activation, the addition of MgO will not cause any increase of strength.

Generally speaking, the authors conclude from the results obtained that the hydraulic properties of the glasses depend on their solubility as well as on the rate of solubility measured in the solutions of the activating agents and on the type of hydrates produced. As to the solubility, they consider the location of the Al ion (whether as a network-forming or a network-changing element) within the glass structure as the decisive factor. The activating action of clinker and lime is traced back to an increase of the lime concentration in the cement solution which will favor a quick decomposition of the glasses and a formation of dicalcium silicate hydrate.

T. Tanaka, T. Sakai, and J. Yamane [27] examined 34 different glasses covering a range of about 26 to 40 percent of SiO_2, 14 to 30 percent of Al_2O_3 and 40 to 52 percent of CaO. The mixing ratio between slag and anhydrite remained constant at 85 to 15. The clinker content amounted to 2.4 and 6 percent.

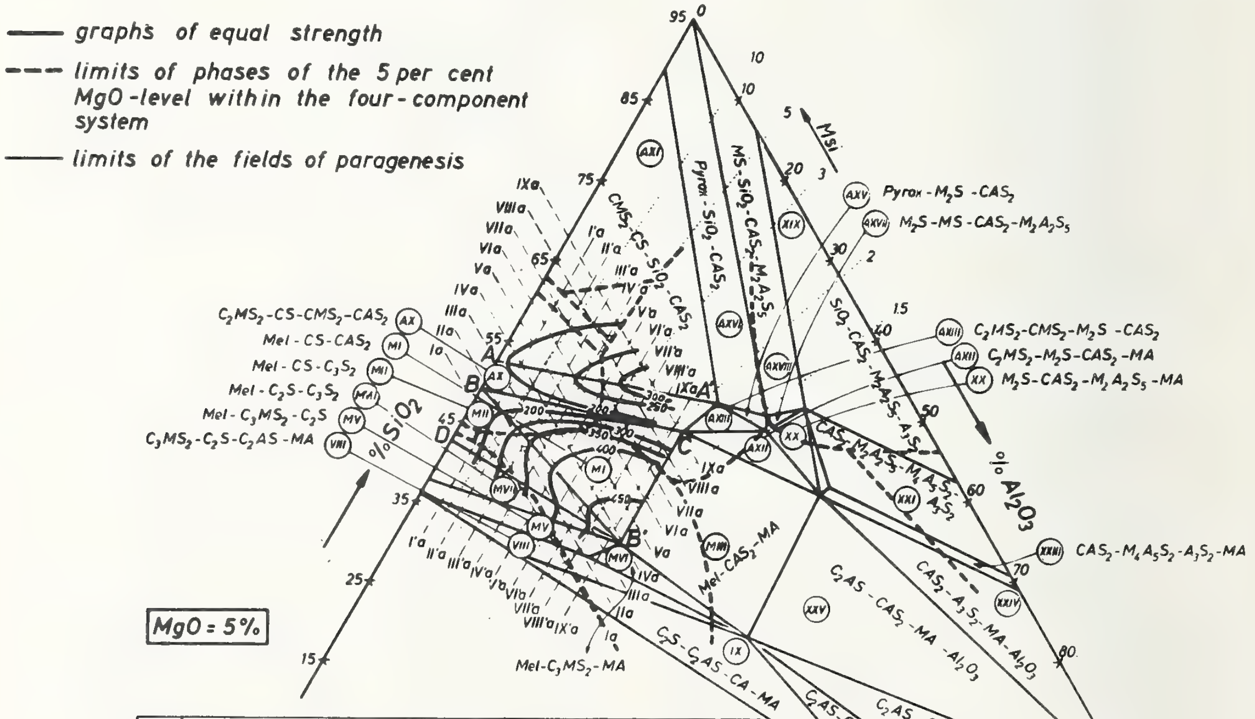
Sulfate-slag cements based on synthetic slags of a composition of 28 to 34 percent of SiO_2, 16 to 20 percent of Al_2O_3 and 46 to 50 percent of CaO delivered strength values more than 80 percent higher than those of conventional portlant cement. The greatest strengths were obtained at the following slag composition: 18 to 20 percent of Al_2O_3, 50 percent of CaO and 30 to 32 percent of SiO_2. At this composition, the sulfate-slag cement produced greater strength than portland cement. The composition of the glass of maximum strength with anhydrite activation was as follows: 18 percent of Al_2O_3, 32 percent of SiO_2 and 50 percent of CaO. For clinker activation, the formula was: 15.5 percent of Al_2O_3, 33 percent of SiO_2, and 51.5 percent of CaO. The field of particularly low strength remained nearly constant for either activating method.

Carrying out similar series of tests, L. Santarelli and G. Goggi [28] tried to determine, in addition to the influence of fluxes such as CaF_2, MnO, FeO, and others, the action of the glass content of the granulates. The favorable influence of a higher glass content as well as of an increased alumina content was confirmed. The flow characteristics of high-aluminous slags and the hydraulic setting power could be improved by small additions of CaF_2.

The most interesting approach to interpreting and explaining the hydraulic properties of the vitreous blast-furnace slags by deductions on the basis of solution theory as well as of confirming the foundations based on the results of the strength development of synthetic slags, was made by S. Solacolu [29]. In view of the finding that the hydraulic properties of the slags will not change proportionately to the oxide composition, he rejects the method of determining the granulated slag by the data and characteristics obtained by chemical analysis as being unsuitable. He believes further the assessing of the energy content of slags on the grounds of structural observation to be incorrect. He considers the difference of energy existing between the unstable glasses and their crystalline devitrification products as being small and unimportant among the factors decisive for the setting power. However, S. Solacolu finds a close connection between the hydraulic activity of vitreous slags and the paragenesis of thermal equilibrium in the crystalline condition. According to the tests, the hydraulic properties are subject to a uniform change within the same paragenesis, whereas in transition to another paragenesis, this change takes place in an inconstant way. S. Solacolu, therefore, regards a heterogeneous constitution of the slag as the basis for assessment of the setting power, supposing the vitreous slags to possess a "quasi-crystalline structure," in which the phases of the crystalline equilibrium are largely preformed according to the rules of a thermal-equilibrium crystallization. Formulae are indicated for calculating the concentration of active and inactive phases on the basis of the oxide compositions. The assessment of the slags is then made according to the hydraulic value of the type of paragenesis determined.

From the eutectics possible in the 20 forms of paragenesis of the four-component system $CaO–MgO–Al_2O_3–SiO_2$ according to T. W. Parker [30], only such types are taken into account that are of interest for blast-furnace slags of hydraulic characteristics. For explanation, figure 7 by S. Solacolu is included here as figure 2. It shows the fields of paragenesis of the thermal-equilibrium phases within the range of the compositions of blast furnace slags (circled points) and the graphs of equal strength values. On the average, slags of the system $MgO–CaO–Al_2O_3–SiO_2$ ($MgO=5$ percent) tested as shown by the figure are located in the fields of paragenesis M I (melilite-wollastonite-rankinite), M II (melilite-wollastonite-anorthite), A X (akermanite-diopside-wollastonite-anorthite) and A XI (diopside-wollastonite-quartz-anorthite). The graphs of same-strength values (S-indices) clearly indicate two maximum points, viz, in the fields of the basic slags along the line *BB′* corresponding to the cleavage plane between M I and M II, and in the fields of the acid slags along *AA′*, the cleavage plane between A X and A XI. The basic slags are separated from the acid ones by a marked minimum. Within the various fields, the strength of the slags changes uniformly, whereas this change takes place inconstantly at the transition from one field of paragenesis to another.

Though a direct comparison is not possible, the diagram drawn by S. Solacolu was compared with the diagram of F. Keil and F. W. Locher, corresponding to the same compositions of slags. In the range of optimum strength, a coincidence is given between the two diagrams. The highest values (Solacolu) and the greatest compressive strengths after 28 days (F. Keil and F. W. Locher) in both diagrams are to be found in the phase of gehlenite (melilite). The examinations by F. Keil and F. W. Locher as well as by S. Solacolu offer suitable possibilities of comparative scientific research for determining the hydraulic character-



Index	Level	Saturation	MgO-Content
DB′	$C_2MS_2-C_3S_2-S_2AS$	$CaO+1.4\,MgO=1.4\,SiO_2+0.27\,Al_2O_3$	$MgO<14.7-0.4\,Al_2O_3$
BB′	$C_2MS_2-CS-C_2AS$	$CaO=0.93\,SiO_2+0.55\,Al_2O_3$	
BC	$C_2MS_2-CS-CAS_2$	$CaO=0.93\,SiO_2-0.55\,Al_2O_3$	
AA′	CMS_2-CAS_2-CS	$CaO+1.4\,MgO=0.93\,SiO_2-0.55\,Al_2O_3$	$MgO<18.5-0.5\,Al_2O_3$

FIGURE 2. *Graphs of equal strength in a section within the fields of paragenesis of the* $CaO—Al_2O_3—SiO_2—MgO$ *system at the 5-percent* MgO *level.*

(According to Solacolu, 1958)

istics of such melts. These are pure glasses which were melted from the initial components until the state of equilibrium was reached. Although clear data are not contained in the works on this point, it must be supposed that the temperature exceeded the liquefying point by a considerable extent. The conversion of the melts into the vitreous state is therefore effected from a condition of equilibrium. The variations from this rule observed by other authors may be traced to different slag temperatures.

It follows from Baldwin's work that with a reduction of temperature, possible variations in this connection will require respective changes of the chemical composition of the slag to maintain a constant viscosity. An application of the interrelations determined for the chemical process of glass manufacture will only be possible in the field of granulated slag under the condition that the temperature of the melt is above the melting point. This takes for granted that the state of equilibrium of the slag solutions has nearly been reached in practical operation and maintained until the moment of granulation. In the manufacture of pig iron, this condition is obtained rather with self-fluxing material than with composed fluxes.

In the latter case the molten slag will not remain in the hearth of the blast furnace long enough to effect homogeneity. By the continuous confluence of differently composed primary melts, the final melt will contain parts of varying chemical composition, which, on granulating, are transferred into the solid state. This feature also explains why previous efforts to draw conclusions from the over-all chemical analysis as to the hydraulic properties of granulated blast-furnace slag made evident certain interrelations, but did not permit one to establish generally accepted rules.

Particular attention must, therefore, be paid to the state of the granulated blast-furnace slag, which virtually characterizes the physical properties of the slag for operation purposes in the manufacture of cement, especially in the production of low-clinker cements (blast-furnace and sulfate-slag cements). The chemical process must be observed additionally.

Importance of the Physical State for Assessing the Hydraulic Properties of Granulated Blast-Furnace Slag

In the report entitled "Slag Cements" which F. Keil gave on occasion of the Cement Chemistry Symposium held in 1952, he subjected every method of assessing the hydraulic properties of granulated blast-furnace slag, which was not based on a chemical analysis, to a critical examination.

During the period under report, A. Lommatzsch [31] has tried to obtain by means of differential thermal analysis a clear understanding of the binding and setting process of granulated blast-furnace slags under sulfate activation. In view of the results of his examinations, he thought them to be of a certain indicative value, attributing the thermal effects observed in the range of 800 to 900 °C to modifications and new formations typical for the hydraulic properties of basic blast-furnace slags.

P. Bornatsch further tried to use calorimetric graphs of heat capacity for assessing different blast-furnace slags. The results of his test, however, are of only limited use, since, despite its low heat conductivity, blast-furnace slag will cool very quickly, and the melting loss conditions prevailing in the coal crucibles cannot be defined. For that reason, the temperatures measured by him are about 100 °C too low. Characteristic conversion points could not be detected. Both works consequently did not contribute to a substantial enlargement of the previous knowledge in the field of blast-furnace slags.

Particular interest is still paid to the method developed in the metallurgical plant of Cockerill at Ougree-Marihaye by R. Feron [32] to classify granulated blast-furnace slags according to the luminous colors they will emit on exposure to ultraviolet rays. The granulated slags glow differently depending on their physical state. Bright red and pink shades are emitted by granulated slags of normal vitreous structure. Granulated slags of high-crystalline structure emit blue and violet colors. Their presence in the granulated slag is evidence that the slag has been melted under unfavorable conditions in the blast furnace or that bad granulating conditions have led to a moderate development of the vitreous state. The strength development of granulated slags, therefore, differs according to the luminous rays emitted.

Based on these observations, the method developed by Féron was found suitable for plant control and has been accepted. His examinations have been confirmed by J. Cleret De Langavant [33]. The importance of the ultraviolet test, also affirmed by him, is restricted by F. Pirotte [34] to granulated slag of the same origin. J. Roquejoffre proved by his tests as well that granulated slags glowing in the range of pink to bright pink exhibit better setting properties, but he believes the method of luminescence is not an exact criterion for assessing the hydraulic properties of granulated blast-furnace slag.

In evaluating the results obtained by Roquejoffre, it must, however, be considered that his examinations differ in principle from those of other observers. Whilst in general dry samples of granulated blast-furnace slags as delivered are tested, Roquejoffre ground the samples into a cement state before analyzing. As his own tests confirmed, the method would hereby lose a great part of its value, as beyond a certain grain size, the particles individually glowing in different colors will no longer be separately perceptible to the eye. Only weak luminescence is then produced, being shifted to brighter, whitish shades.

Considering the different opinions the various observers have had about the method of fluorescence, this method has not met with the widespread adoption hoped for. Its advantage, however, is to be seen in the ease of its application.

The luminous colors appearing on the grains of granulated slag are dependent not only on the incorporation of color centers, but presumably also on the type of prevailing ions, ion compounds, and lattice complexes as well as on their coordinating system. On the other hand, the more-or-less vitreous state of granulated blast-furnace slags reveals the condition exhibited by the solution at the point of solidification by fast cooling prior to granulating.

Our own experiments in the Research Institute for Blast-Furnace Slag at Rheinhausen showed that the differently fluorescing grains of granulated slag are not only dependent on different chemical and mineral compositions, but that they also exhibit various structures and inclusions which are due to varying temperatures and viscosity conditions during the formation of the individual particles of the melt and are, at the same time, indicative of the degree of reduction reached.

The radiographic and microscopic examination of the fluorescence of the differently glowing particles of granulated blast-furnace slag led to a subdivision into a high-aluminous and a high CaO and MgO group (see figure 3).

The granulated slags of hydraulic value with a high-aluminous component emit yellowish-red colors, and those of the lime-and-magnesia series exhibit a pink fluorescence. Between them and the clearly violet or brightly blue glowing crystalline particles exist manifold transitions. The mineral content and the state of aggregation of these transitions as well as of the imperfectly reduced grains glowing dark violet to black violet or blue to black can be seen from the table.

The main components of the high-aluminous group are high-aluminous melilites and wollastonites in addition to small quantities of merwinite. The CaO-MgO group is characterized by orthosilicates (merwinite, dicalcium silicate, monticellite) and high-magnesia melilites. Thus, the pink and blue glowing particles of granulated slag possess a predirected arrangement of ions

High Al_2O_3-content (as per chemical analysis)		Granulated Slags	High CaO (MgO)-content (as per chemical analysis)	
Mineral composition of the fluorescent particles microscopically and radiographically determined	Luminescent color Microscopic analysis of fluorescence	States of aggregate (microscopic examination)	Luminescent color Microscopic analysis of fluorescence	Mineral composition of the fluorescent particles microscopically and radiographically determined
$2CaO \cdot Al_2O_3 \cdot SiO_2 + 2CaO \cdot MgO \cdot 2SiO_2$ Melilites (high-gehlenite mixing links) beside: Ca(Mg) orthosilicates CaS, some wollastonite occasionally rankinite	pure violet	completely crystalline crystals >1μ (partly little glass)	pure blue (strongly glowing)	Orthosilicates: $3CaO \cdot MgO \cdot 2SiO_2$ merwinite ± monticellite $CaO \cdot MgO \cdot SiO_2$ beside: high-åkermanite melilites, little glass, rankinite and wollastonite
	bright violet to lilac white	many crystal separations<1μ of much or less glass	bright blue to bluish white	
Al_2O_3 increasing —— SiO_2 increasing Melilites (high-gehlenite) beside orthosilicates and some pseudowollastonite, occasionally rankinite CaS preferably dissolved in glass	red violet[x] red (carmine) yellowish red red yellowish brown – red brown to brown[xx]	vitreous with many or less inclosures of single crystals, crystal aggregates, crystal cells and dispersed Fe (Mn)-oxides	marine blue[+] bluish grey grey pink pink bright reddish grey brown[xx] brown pink to brown	Increasing C_2S Orthosilicates + CaS (merwinite prevailing) beside high-åkermanite melilites, little rankinite and pseudowollastonite CaS preferably crystalline separated SiO_2 increasing —— CaO increasing
as above plus C (coke) residues, however, Fe-Mn-oxides finely dispersed and oxidated	black brown	vitreous metal oxides strong oxidation	velvet black	as above plus C (coke) residues, however, Fe-Mn-oxides finely dispersed and oxidated
	brownish black violet	additional crystal inclusions	grey blue black	

[x] Violet shade due to crystal cells not clearly perceptible by microscopic and radiographical examination

[+] Percentage increases with storing

[xx] Brown or grey brown shade due to a stronger absorbing power of the glass in consequence of finely dispersed metal oxides and carbon

FIGURE 3. *Determinable characteristics and mineral separations of luminescent particles of granulated blast-furnace slag.*

indicative of insular silicates. In the particles glowing in the range of yellowish-red to violet, there are, additionally, some weak networks of anion complexes.

As demonstrated by microscopic examination, the transitions observed at each series are to be traced back to the luminescence of crystal centers, which, however, are no longer perceptible radiographically. Further variations of the intensity of the luminescent colors depend on the state of the grains of the granulated slag. Highly porous and finely foamed grains emit colors of bright shades, whereas solid compact ones will glow darkly. Bright luminescent colors may also be changed into dark and black shades by incorporation of carbon pigments, finely dispersed iron particles, or ferrous and manganic oxides. Thus, the luminescence of granulated blast-furnace slags reveals not only their vitreous content, but simultaneously the degree of reduction of the slag solutions reached in the melting process.

The distribution of the crystal inclusions as well as the crystal aggregates of the bright fluorescent grains of granulated slag depends on whether they had already precipitated before granulating or whether they were formed only in the process of granulating. In this way, the microscopic observation of the fluorescence of ground particles of granulated slag permits further an evaluation of the method of granulating.

For determining the hydraulic value of differently glowing particles of granulated blast-furnace slag, a granulated slag was analyzed by its various parts of luminescence, and slag of each luminescent color was separately ground together with 30 parts of clinker and 5 parts of calcium sulfate to form an experimental cement of a specific surface area of $2{,}900 \pm 50$ cm^2/g (according to Blaine). For comparison, a mixture composed of clinker and quartz sand was prepared. The strength test of miniature prisms ($1 \times 1 \times 6$ cm) according to Keil gave the following values:

Neutral test and experimental cements of the fractions of luminescence	Bending tensile strength in kg/cm^2				Compressive strength in kg/cm^2			
	after a period of . . . days							
	2	3	7	28	2	3	7	28
65 percent quartz sand 30 percent clinker 5 percent calcium sulfate	6	8	10	15	34	41	48	63
Violet	5	8	11	18	35	45	60	95
Blue	9	9	19	45	49	56	93	200
Dark pink (gray-brownish pink)	15	29	50	83	82	134	242	414
Yellowish red (brick red)	15	25	54	83	80	126	231	430
Bright pink	16	26	50	80	97	144	266	437

The experimental cements are arranged according to the development of the 28-day compressive strength. As can be gathered from the table, the hydraulic components of value in the granulated blast-furnace slags are represented by the brightly glowing particles, whereas the blue and violet glowing grain fractions are scarcely of any influence on the strength development, particularly of the initial strength.

As the determination of the cement strength must still be regarded as the most reliable method of assessing the hydraulic value of granulated blast-furnace slag, the ultraviolet test suggested by Feron figures as a suitable rapid way of examination for assessing and classifying granulated blast-furnace slags. However, for quantitative indications, the determination of the percentages of the different fractions of luminescent colors of granulated slags will be required.

Such particles of granulated blast-furnace slags, separated by screens of 0.09 and 0.06 mm according to their fractions, were microscopically counted as to their fluorescence. The determined percentages by volume of the particles of granulated slags glowing in the range of pinkish red-reddish brown, being glasses, were put in comparison with the strength values of slag cements according to DIN 1164, since the vitreous content of granulated blast-furnace slag has always been considered as a coefficient of quality. As, from experience, the hydraulic value of the dark brown glowing particles of granulated slag is lower than that of the brightly glowing grains, the former were only evaluated by half of their percentage for the sum of the vitreous components. The existing interrelations are graphically shown by figure 4.

The reproduction at the left compares the development of compressive strength of the cements made of granulated blast-furnace slags with the CaO/SiO_2 ratio of the granulated slag. An evident relation between these two values does not exist.

The figure reproduced at the center shows the dependence of the strength development of cements on the percentage of red colors under exposure to ultraviolet rays. The red colors contain the luminescent fractions pink, yellowish red, and half of the dark brown. The points indicating the individual granulated blast-furnace slags are further characterized in the figure by their CaO/SiO_2 ratios.

It appears from the drawing that the red colors of granulated slags emitted under exposure to ultraviolet rays, as well as the chemical composition characterized by the CaO/SiO_2 ratio, have a special bearing on the strength development, i.e., on the hydraulic setting power of granulated slags. Assessing the granulated blast-furnace slags by one of these two factors only will not furnish a clear result. The combination of the physical factors with the chemical data, as indicated by the right-hand section of figure 4, however, gives an excellent picture of the inherent natural laws.

Thus, the hydraulic characteristics of granulated blast-furnace slags are dependent on both the chemical composition and the physical properties of the slags. Most frequently, the CaO/SiO_2 ratio is chosen as representative of the chemical composition. The indicative value of the physical properties is represented by the glass content of the granulated slags, which results from temperature, viscosity, and conditions of granulating.

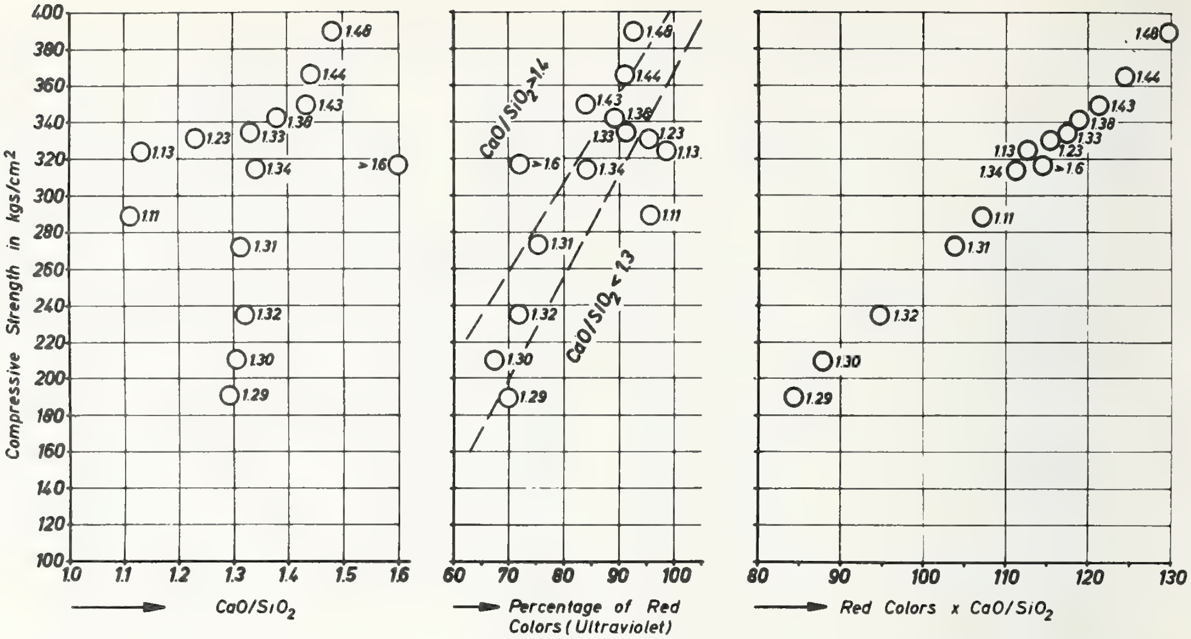


FIGURE 4. *Interrelations between* CaO/SiO_2 *ratio, fluorescence, and compressive strength.*

It can be gathered from the microscopic examination of fluorescence that the glass content should preferably be replaced by the content of red-glowing color fractions contained in the granulated slags. Contrary to the glass content determined by microscope, the microscopic analysis of the fluorescence makes it possible to identify glass portions of different hydraulic action. For granulated slags melted from composed blast-furnace ores and fluxes, the red colors found by analysis of the fluorescence give a clearer picture and may consequently be regarded as the hydraulically effective glass content of the granulated blast-furnace slags. Thus, a clear determination of the hydraulic behavior of granulated blast-furnace slags will be possible at the present state of knowledge, if both the physical conditions and the chemical composition of the granulated slags are taken into account.

Manufacture and Characteristics of Slag Cements

Slag cements are classed among mixed cements. They are made by grinding the components clinker, granulated slag, and gypsum.

Common and Separate Grinding

In the decades past, collective grinding generally prevailed due to the mixing methods not being so far advanced. It was then only the question of an interrupted or a closed cycle. General data on the advantages of one system against the other cannot be established, as either system has its own advantages.

The combination mill, as mainly used in former times, proved quite satisfactory for grinding materials of uniform grinding characteristics. It is, however, too rigid for working components of different grinding hardness and will tend to an overgrinding of the light components, which may be of disadvantage, decreasing both the mill output and the quality of cement. For such raw materials, a superiority of the separator mill is given over the combination mill.

Dealing with this question, Boerner [35] succeeded in proving that, due to its selective method of working, the separator mill will grind the denser clinker species more finely than the less dense granulated slags. In addition to a satisfactory grinding capacity, an improvement of the quality of the resulting cements can also be recorded. This grinding method further offers the advantage of a greater invulnerability against an incorrect mixing of the material to be ground or against varying operating conditions.

In the manufacture of cements consisting of several components, as is the case with slag cements, it is the question, in recent times, of first grinding the individual components separately and then mixing them intimately. The advantage of separate grinding lies in the fact that each component can be ground to the most efficient grain size required for obtaining the optimum hydraulic properties. This system appears useful for the manufacture of cements derived from components of different grinding properties as well as in such cases when, owing to its chemical composition or to its granulating conditions, the granulated slag exhibits only a low hydraulic setting power.

By research on high-magnesian slags, N. Stutterheim [36] succeeded in proving the particular value of separate grinding for the manufacture of slag cements. The resistance to grinding is stronger for granulated slags containing MgO than for the clinker used for activating.

By collectively grinding the clinker and the granulated slag in the proportion of 1:1, the concrete made of this slag cement exhibits a slower initial setting rate than a corresponding concrete prepared with portland cement. The resulting decreased development of heat renders the slag cement particularly suitable for the construction of dams. Two dams have already been built with satisfactory results in South Africa by means of such slag cement containing high-magnesian granulated slag.

His examinations of separate grinding of the components proved that, with high-magnesian granulated slag containing between 13 and 20 percent of MgO and between 38 and 28 prcent of lime, the effect of magnesia on the hydraulic setting power of the granulated slag was not as strong as that of corresponding CaO and alumina contents. Such MgO-containing granulated slags will, even at a finer grain of the slags, influence in a positive way only the final strength of cements. However, an increase of the specific surface of the clinker component from 3,200 to 5,000 cm^2/g will result in a substantial improvement of the initial strength of slag cements. The examinations carried out by Stutterheim thereby demonstrate that, with the purpose of developing most favorable strength values, a separate grinding should be preferred to a collective one for slag cements of such a composition.

The advantages of a separate grinding are further enlarged by L. Blondiau [37], who states that slag cements manufactured by separate grinding will, on long storage, normally be less sensitive to moisture than collectively ground slag cements.

Separate grinding is therefore of particular interest for the manufacture of mixed cements, the more so as, according to Horn [38], a reduction of the grinding cost may also be counted on.

Considering the rapid progress of technique, particularly in the field of homogenizing, it may be expected that the greatest attention, also from the standardization aspect, will be paid to the problem of separate grinding in the years to come. The advantages of pneumatic homogenizing have already been utilized in Germany and some other countries for the regulation of constant qualities of cement.

Composition and Characteristics of Slag Cements

The considerable progress experienced in the field of mechanical engineering, combined with an enlargement of knowledge of the factors acting on the hydraulic properties of slag cements has contributed to an increase in quality of slag cements. The special properties the granulated slag will impart to cements made thereof, as well as the strength formation, were improved. Both an increase of the percentage of granulated slag in cements and an improvement of their hydraulic properties resulted in a more favorable development of the relation between bending tensile strength and compressive strength, a reinforcing of the setting, a decrease of heat formation, and an increase of the resistance to chemicals. In contrast a similar uniform development of the strength formation depending on the content of granulated slag could not be established.

The interrelations existing in the system clinker-granulated slag-gypsum have been examined by W. Kramer [39] in the restricted field of slag cements. It was found out that a proportional relation between the percentage of granulated slag and the strength development of cements must not necessarily be given. As to the compressive strength after 7 days, the same values were obtained with low-clinker cement mixtures (about 20 to 30 percent clinker) as with high-clinker cements (clinker content exceeding 60 percent).

By tests of the latent setting power of granulated slag, R. Stumper and W. Schumacher [40] found as well, that at a constant grain size the characteristics of slag cements will not be subject to change at clinker contents varying from 30 to 70 percent. They stress that the fine grain size is of essential influence on the strength development of slag cements. They further conclude that the mechanical strength of a slag cement, the material composition of which is known, may be regarded as the sum of the individual strength values of the base components, clinker and granulated slag.

W. Kramer and F. Schroeder [41] point to the special influence exerted by the mineral composition of the clinker on the strength formation of low-clinker slag cements. They emphasize that, for an efficient development of the hydraulic properties of low-clinker slag cements, it will be necessary to adjust the composition of the clinker to that of the granulated slag.

The influence of the material structure of the clinker on the characteristics of slag cements has further been examined by L. Blondiau [42] and H. Sopora [43].

In agreement with the tests made by Stumper and Schumacher, Sopora demonstrated that the strength formation of high-clinker slag cements will be dependent on the strength of the clinker, whereas the compressive strength is almost proportional to both the C_3S content and the C_3S/C_2S ratio of the clinker. Yet, Blondiau could not prove with certainty such an unequivocal interdependence by his tests.

For converting magnesium granulated slag, the examinations carried out by N. Stutterheim and R. W. Nurse [44] are of particular interest.

They showed that at a MgO content up to 18 percent, the magnesia does not appear as a free compound, but as a silicate compound which will not affect the constancy of volume of the slag cements made thereof. The strength formation, however, experiences lower values at early tests as compared with that obtained with portland cement, because the effect of the MgO content does not match the action of CaO and Al_2O_3. The special advantages of separate grinding for the development of the initial strength of cements made of high-MgO slags have already been referred to.

Particular importance is attributed to the Al_2O_3 content of the granulated slag for the development of the initial strength of slag cement, as already known from previous tests made among others by R. Grün and F. Keil [45]. Such high-aluminous slags are further characterized by a sulfate activation sensitivity. They form the basis of sulfate-slag cements.

W. Kramer [46] reported on the technological characteristics of sulfate-slag cements, as manufactured in Germany. The point detected by him referring to the high resistance of this species of cement to aggressive water—especially sulfate water—was confirmed by L. Blondiau [47] on the grounds of practical experience. Contrary to concrete tubes made of high-CaO cements, concrete tubes manufactured of sulfate-slag cement did not experience any corrosion despite a flow for many years of waste water having a high content of SO_3 and SO_4 ions and notwithstanding the concentrating of H_2S above the waste-water level.

W. Ruopp and T. Kohlhof [48] reported an extremely favorable experience while building a dam in Germany. Concrete made of sulfate-slag cement in combination with coarse aggregates exhibits a particularly low heat generation, a small shrinkage, and high initial strength, which render it most suitable for the use of inclined-plane boarding.

B. Wentz [49], L. Blondiau [50], Th. Alix [51], and S. Haerig [52] give reports of satisfactory results obtained with slag cements in practical building, among others in the field of road and airport construction.

Some of these works particularly emphasize the good results obtained by using blast-furnace lump slag as an additive. Since blast-furnace slag acts as a supplier of CaO to the aqueous stage of the cement solution, it seems to have a favorable bearing on the strength of the concrete made thereof and of slag cement.

Hydration Processes

The process of hydration of granulated slag is by far not as clear as that of portland-cement clinker. Nevertheless, several works dealing with a restricted section, produced a series of revealing results.

At the contact with water, slag releases Ca ions. At the surface of the grains of slag, acid hydrate layers will separate, according to J. D'Ans and H. Eick [53] and also swollen, water-impermeable aluminum oxyhydrate gels as found by S. Chatterji and D. Lahiri [54]. These impermeable hydrates dissolve as soon as the CaO concentration reaches a sufficiently high level. The delivery of calcium ions by the granulated slag to the solution may then continue.

According to S. Chatterji and D. Lahiri, mixtures of calcium aluminate hydrate and hydrogarnet will form upon the hydration of grains of basic slag, whereas gehlenite hydrate will form with low-calcium slags for which the Al_2O_3/SiO_2 ratio is less than one. On the whole, the formation of hydrogarnets appears to be dependent on high-calcium and calcium-supersaturated solutions. (F. H. Dörr [55] and C. H. Schmitt [56].)

For calcium silicates, the calcium oxide concentration of the solution is decisive for the kind of product formed. If the CaO content exceeds 0.020 mole/l, formation of CSH–II (according to Taylor)$=1.7$–$2.0CaO{\cdot}SiO_2{\cdot}aq.$ will be the rule. At a lower concentration, CSH–I (according to Taylor)$=0.8-1.5CaO{\cdot}SiO_2{\cdot}aq.$ is in equilibrium with the solution. This CSH–I approaches tobermorite in its structure. It is the function of the lime-supplying agent to always maintain in suspension as much lime as is required for the hydration process to develop without interruption. The fact that blast-furnace slag delivers Ca ions when agitated in water, whereas it absorbs Ca ions from lime water, is thereby also explained.

In the former case, the CSH–I is in equilibrium with the aqueous phase. Delivery of Ca ions to the solution will not be sufficient to bind the silicate hydrate of higher calcium content. In the presence of lime water, however, these conditions exist, and for that reason, the CSH–II will now be in equilibrium with the aqueous phase.

As to the process occurring in the activation of blast-furnace slags by means of anhydrite and clinker, H. Kuehl [57] has supplied a plausible explanation. The products resulting by this process are ettringite, ettringite monosulfate, aluminum hydroxide, and secondary calcium silicate hydrates.

In the hydration of silicate glass, the hydrates formed will be very similar in their crystalline structure to zeolites, e.g., the three-dimensional combination of SiO_4 tetrahedrons with AlO_4 tetrahedrons. It must be considered in this connection that the zeolites represent pure hydrates, whereas the designation of "hydrates" for the other products is not quite correct. In the former case, H_2O appears as a molecule, whilst in calcium silicate hydrates, this type of bond occurs only in part. As reported by H. O'Daniel [58], it was found on the analysis of afwillite, hillebrandite, and tobermorite, that the hydroxide is not quite without a tetrahedron bond in these compounds. Upon his judgment, bridges may, in theory, thereby be given from Si to Si by both an oxygen and oxygen-hydrogen way.

These types of bonds are of particular importance to the formation of the structure of the binding agent. The silicon-oxygen groups constitute components of higher resistance to chemical influences than hydroxide bridges, which may easily be separated in the presence of concrete-affecting anions of corrosive waters. The stability depends on the frequency of incorporation of such Si-O groups.

Tests made to this effect by the Research Institute for Blast-Furnace Slags at Rheinhausen have shown that, with slag cements, the quantity of OH groups to be incorporated is dependent on the composition. At a lower clinker content, the quantity of OH ions in cement solutions is substantially reduced. This explains the satisfactory stability of cements rich in blast-furnace slag against the influence of chemically aggressive materials.

Summary

The chemical process, temperature, and viscosity are important factors in the use of slag in blast furnaces. Interrelations exist between them, rendering it possible to regulate the reactions taking place in the stack and hearth of the furnace by changing the chemical composition of the blast-furnace slag for the most favorable working conditions. The MgO and Al_2O_3 content of the slag plays an essential role, as well as the CaO/SiO_2 ratio.

The chemical process and the physical state are decisive for the development of the hydraulic properties of granulated slag. For that reason, a regulated working of the slag is of advantage not only to the metallurgical processes taking place in the blast furnace, but also to cement manufacture. The chemical activity is already determined by the slag melting. The vitreous state of granulated slag is regulated by the temperature and viscosity of the molten slag at the granulating process on the one hand, and by the cooling conditions, on the other, depending on the granulating installation.

Comparative tests of the action of the chemical composition of granulated slags on their hydraulic characteristics are only possible if the temperature of the melts prior to granulating is above the liquefying point. Differences of results may be due to non-observation of this precaution in some tests.

The works carried out during the period under report revealed the interrelations existing between the tapping temperature, the CaO/SiO_2 ratio of the blast-furnace slag, and its strength development under alkaline activation. They further indicated the influence of a higher MgO or Al_2O_3 content on the hydraulic properties of the granulated slags. Contrary to the action of MgO, an increased concentration of alumina will improve the reactivity of granulated slags. The cements made thereof will, under alkaline as well as sulfate activation, experience an increase of strength, particularly at the initial stage.

As to slag cements, there are determined areas of preferred strength development under both activating methods. The existence and the location of strength maxima strongly suggest a heterogeneous phase constitution of blast-furnace slags. The interrelations between the hydraulic properties of blast-furnace slags and the thermal equilibrium of paragenesis at the crystalline state offer a satisfactory assessing method for slags, the tapping temperature of which is higher than the melting temperature.

However, in practical operation, this condition is not always fulfilled. For that reason, special attention should be paid to the glass content of granulated slag in addition to its chemical composition. The methods examined in the period under report are explained. A preferable indicative value which is particularly suitable for practical operation, because of its ease of application, is attributed to the test under ultraviolet light. A quantitative analysis of the red colors of granulated slags as components of the hydraulic effect is obtained by means of a microscopic examination of fluorescence which, combined with the chemical data of granulated slags, is a sufficient basis for assessing the hydraulic value.

The interrelations existing in the development of the technical properties of cement—particularly of the strength values—in the field of slag cements give evidence of the prevailing characteristics of the clinker in high-clinker types. In the low-clinker slag cements, the granulated slag is decisive for the hydration process and the strength development. The action exerted by the mineral structure of clinker on the strength development of slag cements may be demonstrated. A completely clear answer to this question, however, has not been given so far.

As for slag cements rich in granulated blast-furnace slag, the latent hydraulic setting power is released only by the alkalinity imparted to the fluid cement phase. The mineral structure of the clinker appears to be of influence on the strength development of this type of cement, particularly at the initial tests. A definite clarification of the interrelations, however, could not yet be obtained during the period under report.

Based on the work under consideration, mention is made of the technical properties of slag cements—especially of low-clinker blast-furnace cements and of sulfate-slag cements—in connection with their use for various constructions.

Concluding, the processes occurring in the hydration of slag cements are dealt with in reference to the literature available. The possibility of forming links between different Si atoms by both oxygen and oxygen-hydrogen bridges, shown by H. O'Daniel, seems to merit particular attention in view of its importance for the stability of cements against attacking chemicals.

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Discussion

Renichi Kondo

The paper by W. Kramer entitled "Blast Furnace Slags and Slag Cements" is particularly interesting to me, as I have been studying mainly in this field. Allow me to bring up some questions on problems that arose during reading the paper.

On the Structure of High-Lime Glass

In his paper, he wrote that "the Al ion of basic melts may only be considered as a network-changing element at temperatures above the melting point," and consequently "the Al ion is maintained as a network-changing element of granulated slag." I understand that his term "network-changing element" coincides with the term "network modifier" generally used in glass study.

My experiments have manifested several indications, however, that the Al ion tended to take fourfold coordination, i.e., to act as a network former [1].[1]

From the determination of the glass-forming range in the CaO–Al_2O_3–SiO_2 system, the limit was found close to Zachariasen's number $n=0.29$, and MgO extended it a little. The n-value is an indication, in the expression A_mB_nO, where A is the network modifier such as Ca^{2+}, and Mg^{2+}, B is the network former such as Si^{4+} and Al^{3+}, while O is O^{2-}.

It seemed possible to substitute Al^{3+} ion for SiO_2 in the form of a tetrahedron. In the CaO–Al_2O_3 system, glass formation occurred only at around $Ca_{12}Al_{14}O_{33}$ where Al^{3+} ion could take fourfold coordination. The melilite series of solid solutions is known as the main component of blast-furnace slag, and in this mineral Al^{3+} and Mg^{2+} ions take fourfold coordination.

Moreover, the thermal behavior of high-lime glass revealed that the replacement of SiO_2 by Al_2O_3 tightened the structure [2]. Figure 1 illustrates the temperatures of the endothermic and exothermic effects in DTA measurements of samples on the join $CaO{\cdot}SiO_2$—$CaO{\cdot}Al_2O_3$.

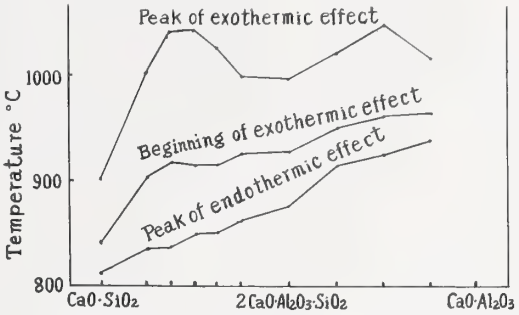

FIGURE 1. *Thermal behavior of glasses in the* $CaO{\cdot}SiO_2$–$CaO{\cdot}Al_2O_3$ *system.*

The effect of the chemical composition may be such that the introduction of CaO breaks the chain of covalent bonds and somewhat lowers these temperatures, while the replacement of SiO_2 by Al_2O_3 produces unsaturated O in $[AlO_4]$ tetrahedra, tightening the structure and raising these temperatures.

There is a test for evaluating cement slag by means of DTA, as mentioned by Dr. Kramer, and the basis for this procedure may partly be explained by the above behavior.

Optimum Composition of Slag for Cement

The results obtained by S. Solacolu are of special interest. He found two peaks of strength in three- or four-component systems and proposed "the quasi-crystalline structure theory" in order to explain this fact. I rather prefer to think from my experimental results mentioned below that the larger peak of strength appearing in the high-CaO region is based on the latent hydraulic property, while the smaller peak in the lower CaO region is due to the other causes, probably pozzolanic action.

The latent hydraulic properties of systematically prepared glasses were already examined in 1952 [1, 3] by us, with special regard to the effect of interaction between the composition of glassy samples and the sort of exciters. This interaction was very significant. For an example, C_2AS glass was evaluated as low in activity in cases such as portland blast-furnace cement, especially that low in clinker, and common sulfated slag cement. It was evaluated, however, as the most desirable glass to use to obtain maximum strength in lime-slag cement or lime-gypsum-slag cement containing much lime as the alkaline exciter. The higher the alumina content in slag, the greater is the hydraulic activity, but at the same time greater amounts of exciters are required. In such a condition, the exciters seem to assist the pozzolanic action of glass instead of acting as catalysts.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Evaluating Methods for Slag

The potential mineral composition of granulated blast-furnace slag may now be estimated by X-ray analysis. Such a study is in progress, mainly by X-ray diffractometer, in cooperation with the members of Committee No. 111 of the Japan Society for the Promotion of Science.

Granulated slag gives a broad halo, the diffraction angle of which changes approximately with its basicity, while with samples devitrified by heat treatment there appear sharp diffraction lines of melilite of various compositions and of other silicates.

This method seemed to be the most promising for the evaluation of slag, because of its swiftness and accuracy. The application of an X-ray spectrometer such as the Autrometer is also under consideration for the rapid chemical analysis of slags.

Grinding Process

It is suggested in Dr. Kramer's paper that "the advantage of separate grinding lies in the fact that each component can be ground to the most efficient grain size required for obtaining the optimum hydraulic properties."

I have tried the substitution of coarsely ground granulated blast-furnace slag for a part of the sand and portland cement with the purpose of improving the characteristics of mortar [4].

It was necessary that the grain size of this additional slag fall between those of sand and cement. The addition of some type of calcium sulfate was also desirable for its action of accelerating the hydration of slag.

The application of this admixture improved the characteristics of mortar such as workability, strength, chemical resistivity, drying shrinkage, efflorescence, etc., and also allowed a reduction in the quantity of cement.

From the experiments described above or made previously, the size distribution of portland blast-furnace cement is desired to be such that the portland cement clinker is in the medium size range with its distribution as narrow as possible and the slag part is divided to extend on either size.

The hydration of cement proceeds chemically much more easily with increasing fineness, but the suitable grain-size distribution tends to act not only for the development of increased strength but also for improving the workability and for decreasing the bleeding and shrinkage.

New Types of Slag Cement

The utilization of slag cements is expected to be enlarged in the near future by the improvement of their characteristics suitable for various usages.

First, I studied methods to determine the optimum content of alkaline and sulfate exciters for the development of strength in sulfated slag cement, and found that the conduction calorimeter [5] and the chemical determination of SO_3 in the extracted liquid [6] are effectively applicable for the purpose. Sulfated slag cement showed a heat-liberation peak of 1.1–1.2 cal/g-hr., having gentle slopes to both sides at about 18 hr as illustrated in figure 2, and the optimum quantity of alkaline exciter might be inferred from the minimum quantity necessary for giving a peak of this definite height and shape. At the optimum value of SO_3 content in the sulfated slag cement, the concentration of SO_3 in the extracted liquid remained approximately constant at 500–600 ppm after 3 days.

The very early 3-day strength of the low-clinker type of portland blast-furnace cement produced in Japan was only about half that of normal portland cement, but it could be improved to be of the same order by further addition of anhydrite up to 5 to 10 percent, without decreasing the long-time strength [4]. The drying shrinkage of the original cement was rather low, but the addition of anhydrite increased the expansion due to hydration by such an amount as to compensate for the drying shrinkage, yet there was no sign of a risk of excessive expansion. K. Okada found that the portland blast-furnace cement revealed a tendency toward lower creep in comparison with the several types of cement, a desirable characteristic in its application for prestressed concrete.

The specimens containing blast-furnace cement sometimes caused remarkable expansion in contact with sulfate solution, but the further addition of calcium sulfate to the original cement remarkably improved the chemical resistivity by the formation of a dense and inactive texture [7].

Sulfated slag cement is expected to be advantageous for the development of the strength of soil cement and lean mortar, both having high

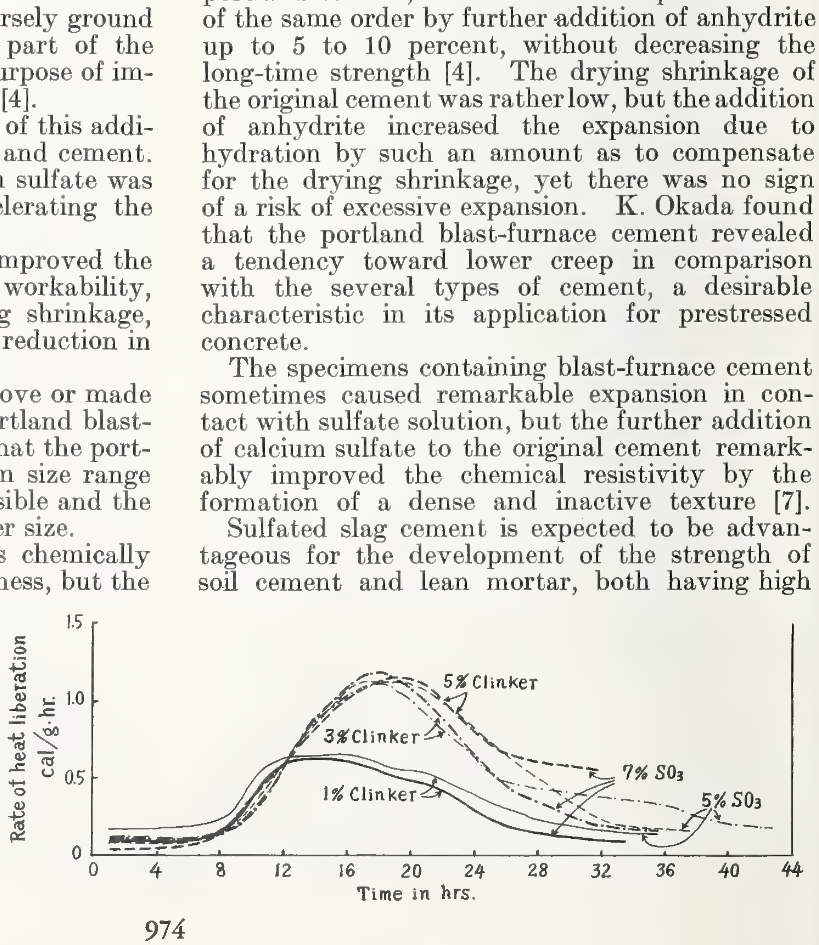

FIGURE 2. *Rate of hydration of sulfated slag cements of various compositions.*

water-cement ratios, as its hydrated products retain much combined water. The optimum content of alkaline exciter in sulfated slag cement increased along with the water-cement ratio and also with the clay content in the mixture. The expansion due to hydration, even with the expansive cement, generally declined together with the water-cement ratio. It would be very desirable if the clay in soil could take part in sustaining the strength as a part of the cement. Possibility of this action was confirmed, provided the quantity of alkaline exciter and calcium sulfate in the cement was greatly increased.

Accordingly, the addition of about 20 percent or more of calcium sulfate appears to make portland blast-furnace cement suitable for soil stabilization. The mixture of lime and calcium sulfate is one of the most desirable additives for the stabilization of clayey soil [8].

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Discussion

H.-G. Smolczyk

First we want to thank Mr. Kondo for the interest he has taken in our paper and for his most interesting contribution to the discussion. I am going to make the following comments:

The modal mineral composition of granulated blast-furnace slag has been determined at the Research Institute for Blast-Furnace Slags for many years by means of X-ray analysis. But aside from the nature and quantity of the slag minerals one obtains only the total content of the entire vitreous phase.

As this method can neither give indications about the different glasses nor about their structure in vitreous slags—and we consider this structure to be the most important measure of assessment for the latent hydraulic capacity—it has not yet been applied for determining the quality of granulated slags. The only usefulness consists in ascertaining to what extent the vitreous constituents have been replaced by more or less hydraulic inert slag minerals as melilite, wollastonite, merwinite (and stablilized dicalcium silicate, if any).

The vitreous part of a commonly used granulated blast-furnace slag is composed of various glasses with different hydraulic values. This fact was first suggested by F. Schröder [1],[1] who deduced it from the wide dispersion of the refractive indices of many samples investigated in the Research Institute for Blast-Furnace Slags at Rheinhausen, Germany.

As it is impossible to separate the various glasses by means of another method, he applied the ultraviolet test for this purpose. He gave instructions to select the different luminescent glasses and to manufacture test cements and determine their strength properties on mortar prisms 1×1×6 cm.

It was thereby possible to prove that granulated blast-furnace slags are composed of vitreous grains with different hydraulic properties.

Further, F. Schröder found that an increase in the concentration of activator particles or an incorporation of minor components (metals or oxides) may reduce or extinguish the emitted luminescence colors. Taking into consideration this kind of change in the luminescent colors he pointed out that, independently from the different melting processes, to a first approximation a number of granulated slags radiate on exposure to ultraviolet light within the same regions of wavelengths (pink, salmon-colored, reddish-brown, dark-brown, blue, and violet).

On the basis of these results he recommended the ultraviolet test suggested by R. Féron [2], J. Cleret de Langavant [3] and P. Pirotte [4], and developed the evaluating method as described by W. Kramer in the paper under discussion.

As far as can be judged from experience available, a granulated blast-furnace slag with normal chemical composition radiates intensively, in the case of a good and rapid granulation, emitting pure red colors. "Pink" is the prevailing color in granulates with Al_2O_3 content <14 to 15 percent and a minor MgO content. The "salmon-colored" portion increases with Al_2O_3 >14 to 15 percent and a greater MgO content. Slag glasses, obtained from relatively cold-blown Thomas pig-iron slags radiate less intensively and the "red" colors change to "grey-brown", "yellowish-brown", "reddish-brown" and "dark-brown". A deficient granulation changes the luminescence colors in the same way.

F. Schröder extended his investigations also on blast-furnace slags high in magnesia. They emit luminescent colors within the same regions of the visible spectrum. Due to the small bivalent

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[1] Figures in brackets indicate the literature references at the end of this paper.

Fe-like ionic-radius (MgO^{++} 0.78 A and Fe^{++} 0.83 A), the emitted colors will be weakened or extinguished in the same way by increasing percentages of MgO.

An X-ray-analytical examination of the minerals incorporated showed different proportions for the "pink" and the "salmon-colored" fractions of the luminescence colors. The ratio of orthosilicates/melilites (+ wollastonite), (i.e., nesosilicates/soro-silicates) is generally >1 for the "pink" and <1 for the "salmon-colored" fraction.

F. Schröder concluded, therefore, that the $[SiO_4]$-network of the "pink" luminescent glasses is extensively dispersed in isolated tetrahedrons of $[SiO_4]$ ($[AlO_4]$), while in the "salmon-colored" luminescent glasses small complexes of tetrahedrons are predominant (double tetrahedrons in melilites and short chains in wollastonite), which means that a first condensation has taken place. Consequently it seems to be possible to obtain indications about the structure of the vitreous constituents of a blast-furnace slag at the moment of their quenching, by means of their luminescence.

As to the question of the type of bond of Al_2O_3 in slag glass, we should like to give the following comment: before being fixed either as a network former or as a network modifier in the crystal lattice, the Al^{3+} ion will take a balanced position between these two possibilities which is then kept frozen in the glass by the rapid cooling.

AlO_4 groups are spots of weakness in the SiO_4 network. With rising temperature the network will break off at these points, due to the different deformation of the coordination polyhedrons.

In addition to the Ca^{++} ions, the temperature acts as a network modifier too. There is no reason to connect this action with any alteration of the coordination number of the Al ions from 4 to 6. It is preferable to assume that within a definite temperature range the actuation of covalence forces can be avoided by the mutual deformation degree of the Si- and Al-coordination polyhedrons, and that in the melt both exist parallel, as isolated groups or small polyhedron complexes. Within definite temperature ranges and up to certain concentrations, one sort acts against another as a sofetening agent or reversely (as in the case of high polymeric substances).

In consequence we come to the conclusion that the luminescence is an important property of a granulated blast-furnace slag concerning the critical examination of the hydraulic capacity.

A number of factors are co-acting to form this property: temperature of the slag, chemical composition, viscosity, and granulation conditions. Their different influence can be demonstrated, and aside from this, the luminescence enables us to obtain information about the structure of the slag glass, which is very important for the latent hydraulic capacity.

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Discussion

G. Malquori, R. Sersale, and P. Giordano-Orsini

While investigating hydration products of basic granulated slags in the presence of activators, we have treated slags with lime solutions and have systematically followed the morphological evolution of hydration products by means of optical and electronic observations. It is impossible to report here in full the results of our researches, but they have already been published in Italian journals [1].[1] We should like, however, to show here some of the micrographs that appear to be of interest.

Table 1 shows the chemical composition of the slags we have employed.

Table 1. *Analyses of slags*

Chemical composition (percent of substance dried at 105 °C)

Slags	SiO_2	Al_2O_3 $+TiO_2$	CaO	MgO	FeO	MnO	S (from sulfides)	Na_2O	K_2O
No. 1	34.95	10.53	46.27	4.07	0.45	1.97	1.68	0.46	0.44
No. 2	35.27	10.86	42.81	4.63	.60	3.47	1.61	.70	.50
No. 3 [a]	34.05	18.27	42.69	4.99	------	------	------	------	------

[a] Synthetic slag sample prepared in laboratory.

Electron micrograph 1 shows slag sample No. 1 (table 1) after treatment with initially saturated lime solution. The observation was made after shaking slag and lime solution for 24 hr. Feltlike masses covering the surface of an original grain and some aggregates of lime crystals showing rhombic section, lying at the boundaries of other grains, are to be seen. The above mentioned feltlike masses are probably to be identified with tobermorite.

As has already been stated [2], at low temperatures (below 100 °C), tobermorite has been recognized in two crystal shapes: large crystal sheets and fibrous or needlelike crystals. In saturated lime solutions—which are in general used in our experiments—fibrous or needlelike growth seems to be promoted.

The role of ettringite in the rapid growth of needlelike crystals has not yet been entirely clarified even for portland cement [3], because of the abundance of these structures in comparison with the normal content of SO_3, amounting to about 2 percent for commercial portland cements.

With regard to blast-furnace slags hydrated in the presence of saturated lime solution, it is to be noted that we have found needlelike crystals,

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[1] Figures in brackets refer to the literature references at the end of this paper.

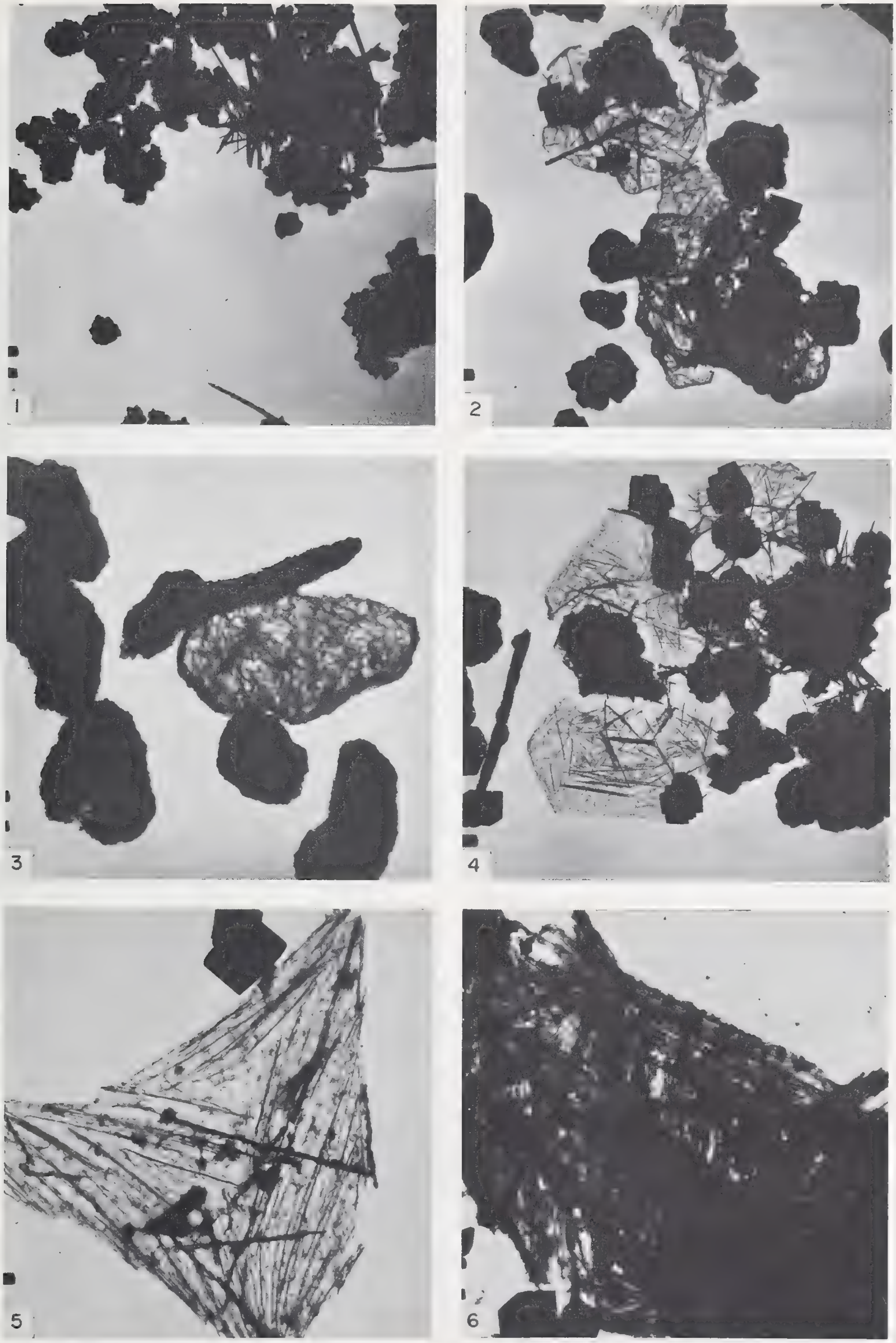

FIGURE 1. *Electron micrographs showing the morphological evolution of hydration products.*

t=time elapsed between sample preparation and the microscopic observation.
T=CaO content of contact solution while preparing sample (mM/liter).

(1) t=24 hr ; T=∼17
(2) t= 5 days; T=∼12
(3) t=60 days; T=∼ 6
(4) t=24 hr ; T=∼21
(5) t= 5 days; T=∼21
(6) t=60 days; T=∼16

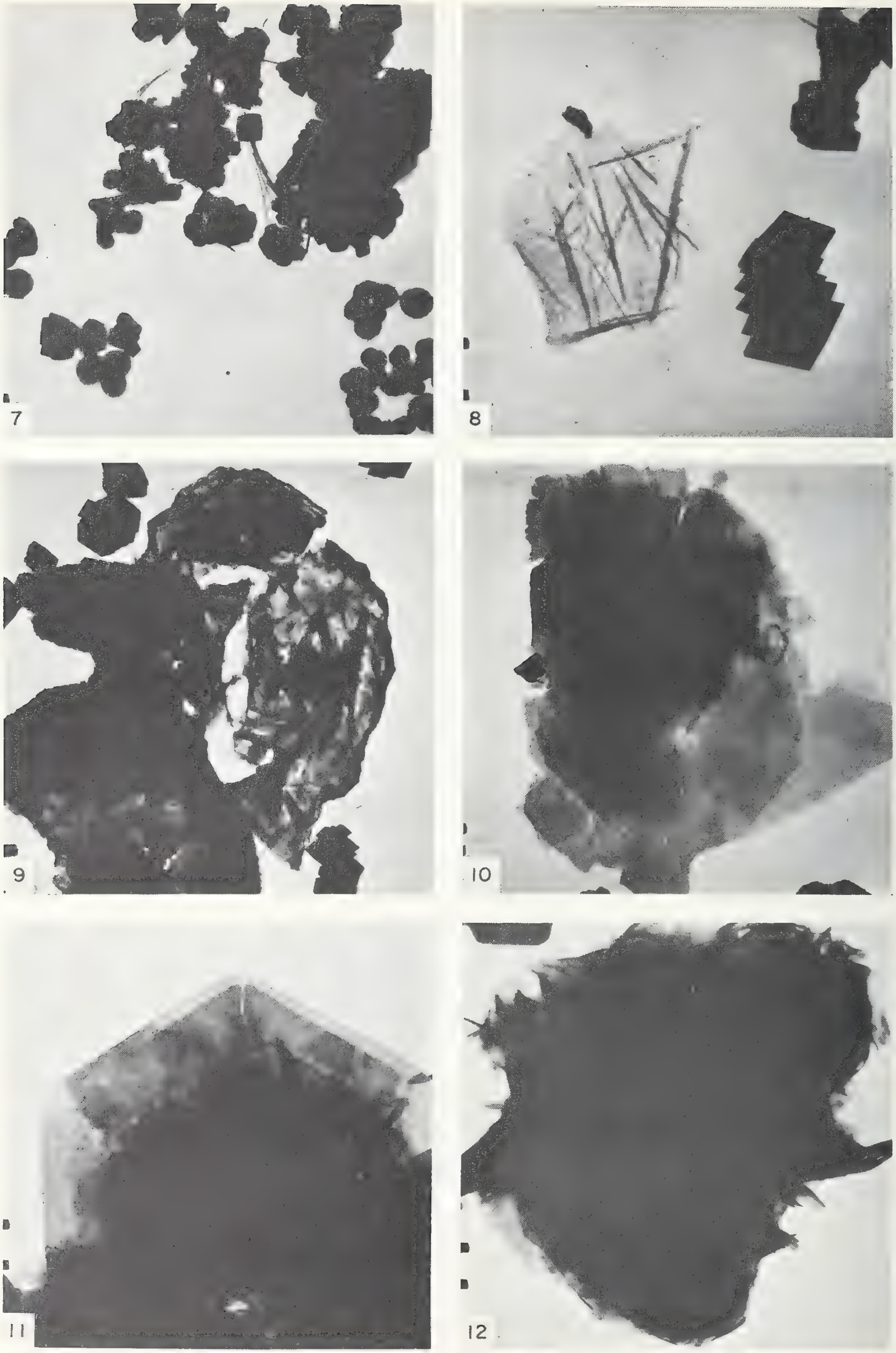

FIGURE 1. *Electron micrographs showing the morphological evolution of hydration products*—Continued

t=time elapsed between sample preparation and the microscopic observation.
T=CaO content of contact solution while preparing sample (mM/liter).

(7) t=24 hr ; T=∼21
(8) t= 5 days; T=∼19
(9) t=60 days; T=∼16
(10) t=24 hr ; T=∼21
(11) t= 5 days; T=∼19
(12) t=60 days; T=∼16

covering the surface of glassy slag grains, for sulfur-free slags as well. This very interesting question will be thoroughly investigated in a following paper.

Electron micrograph 2 shows, after five days' shaking, the same feltlike masses we have observed in micrograph 1, lying on not yet well-contoured thin hexagonal plates.

Micrograph 3, after 60 days, shows only a thickening of the structures in micrograph 2. It is to be noted that the evolution from picture 2 to 3 occurs in an unsaturated lime solution.

Micrographs 4, 5, and 6 refer to the same slag sample No. 1 (table 1). The initial lime-slag ratio is higher (10 percent) than it was in the former case (3.3 percent). Observations were made, as usual, after 24 hr, 5 days, and 60 days.

Micrograph 4 shows the same feltlike masses (tobermorite) as micrograph 2, lying, this time too, on thin, well-contoured hexagonal plates. Micrograph 5 clearly shows the above mentioned feltlike masses (micrographs 2 and 4).

Micrograph 6 shows the thickening of the structures of 5. The evolution from micrograph 4 to 6 occurs this time in a constantly saturated lime solution.

Micrographs 7, 8, and 9 refer to slag sample No. 2 (table 1), after treatment with lime solution. The initial lime-slag ratio equals 6.6 percent. Micrographs have been made, as usual, after 24 hr, 5 days, and 60 days shaking.

Micrograph 7 shows the beginning of formation of feltlike masses (but not so advanced as for sample 1 under the same experimental conditions (micrograph 1)) and the presence, too, of $Ca(OH)_2$ either as spherulites or as crystals showing rhombic section. Micrograph 8 shows tobermorite that, initially a feltlike mass, exhibits now a needlelike structure. This time, too, hexagonal plates of calcium aluminate hydrates support these needles. Lime crystals, as well as residual feltlike masses are still present. Micrograph 9 shows the thickening of the structure in micrograph 8. Hexagonally contoured plates supporting needles are now well shaped. The evolution from micrograph 8 to 9 occurs partly in a saturated lime solution and partly in a solution below saturation. Small lime crystals, as micrograph 9 shows, are to be attributed to lime deposit during specimen preparation.

Micrographs 10, 11, and 12 refer to sample 3 (table 1) after treatment with lime solution. The initial lime-slag ratio equals 6.6 percent. Observations were made after 24 hr, 5 days, and 38 days.

Micrograph 10 shows a semi-transparent contour, lying at the boundaries of a slag grain, which is to be identified with hexagonal calcium aluminate hydrates. Micrograph 11 shows very well-grown ordinary hexagonal plates.

Micrograph 12 shows feltlike masses, which are to be identified with tobermorite, and hexagonal plates of calcium aluminate hydrates. The last observation refers to bottom materials in contact with no longer saturated lime solution. The abundance of hexagonal aluminate plates is to be attributed to the high alumina content of this slag sample (No. 3, table 1).

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Discussion

H. Williams and S. K. Chopra

Indian slags are characterized by low CaO/SiO_2 and SiO_2/Al_2O_3 ratios and as such are not considered good for making supersulfated or slag-sulfate cement (references 26 and 27 of the above paper). While determining the composition of the glass of maximum strength, Tanaka (reference 27) and his co-workers kept the mixing ratio between slag and anhydrite constant at 85 to 15. Many other workers have employed more or less similar ratios for the activation of synthetic glasses and industrial slags. However, the data given below show that by carefully working out the optimum conditions of activation in the light of observations made by Keil and Locher (reference 26) and by Blondiau [1][1] regarding the quantity and solubility of $CaSO_4$ in relation to the contents of lime and soluble alumina, strengths can be raised substantially so as to make the slags acceptable for industrial exploitation.

The slag found most suitable for making portland blast-furnace cement in an earlier investigation [2], and having the ratios of CaO/SiO_2 and SiO_2/Al_2O_3 as 1.11 and 1.47, respectively, also proved best for sulfate activation. The trial cements prepared by mixing slag, burnt gypsum (optimum temperature 750 °C) and clinker in the proportions usually employed in the manufacture of supersulfated cement did not show good strength development in 1-in. cubes prepared from the cement pastes of normal consistency. The determination [3] of unreacted $CaSO_4$ in the set cement showed practically complete depletion of $CaSO_4$ in three days time. In view of these results and the high alumina content (22.6 percent) of the slag, the effect of increased amounts of $CaSO_4$ on the development of strengths was studied, and the results are shown in figure 1. There was a general increase in strengths and the optimum amount of $CaSO_4$ appeared to be 20 to 25 percent. The trial mix K55 having proportions 70/25/5 was considered best for

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[1] Figures in brackets indicate the literature references at the end of this paper.

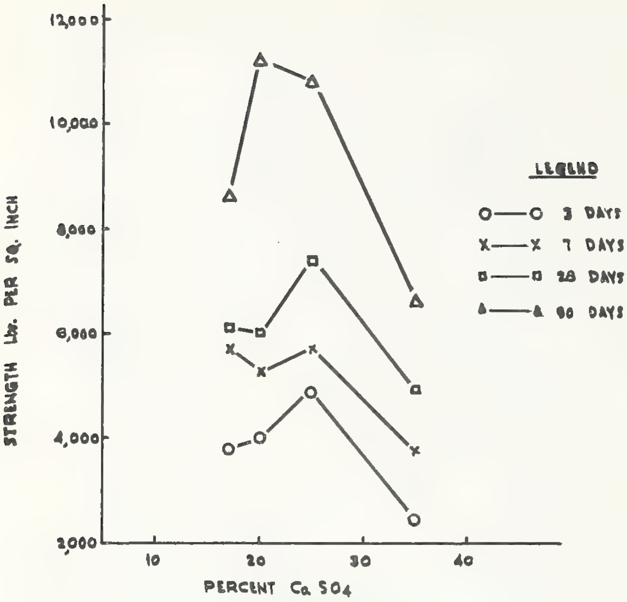

FIGURE 1. *Effect of calcium sulfate content on the development of strength.*

making supersulfated cement (the optimum amount of clinker was found to be 5 percent). The physical properties of the cement (4,000 cm^2/g) compare favorably with some of the cements being produced elsewhere [4]. For example, the strengths of 1:3 mortar cubes (vibrated) were found to be 2,400, 3,500, 6,330, and 11,600 $lb/in.^2$ at 3, 7, 28, and 90 days, respectively. A 1:2:4 concrete with W/C ratio of 0.6 showed a strength of 6,500 $lb./in.^2$ at 28 days. Grinding the cement finer is likely to result in still better early strengths. There was practically no expansion in 1:3 mortar bars on storage in water for 9 months, and examination of the set cement products by chemical methods, DTA, and X-ray spectrometer analysis (2 θ from 5 to 50 °) have shown that there is no likelihood of any delayed expansion.

That the optimum amount of activator is 20 to 25 percent is also borne out by comparing the hydration products of the cement K55 with those of the cement K44 containing an insufficient quantity of $CaSO_4$ (i.e., 17 percent.)

DTA of the cement K55 showed the formation of high sulfate form of sulfoaluminate (ettringite) at all ages from 3 to 90 days. The magnitude of the endothermic peak at 160 °C showed that ettringite was present in the largest quantity at 28 days. Very good agreement of the X-ray powder data of the 28-day-old sample (table 1a) with the published data [5], indicates that the composition of the cementitious phase is almost $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$. At all other ages the ettringite phase seems to have a lower SO_3/Al_2O_3 ratio. The longest spacing at these ages occurs at 9.71 A, and according to Midgley and Rosaman (paper III–S2, this symposium) the phase has an SO_3/Al_2O_3 ratio of more than 2.58. Since complete X-ray data is not available, it is difficult to discount the existence of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}aq.$ in solid solution with $3CaO{\cdot}Al_2O_3{\cdot}3Ca(OH)_2{\cdot}aq.$, which has been reported by Nurse [6] as the cementing solid in set pastes of supersulfated cement prepared from slags of relatively low CaO/SiO_2 ratios. The lines at 5.02A, 2.86A, 2.55A and 1.82A in the 7-day-old sample probably show the presence of dicalcium aluminate hydrate.

The differential thermal analysis of the set trial cement K44 showed only one endothermic peak at 150 °C both at 3 and 7 days. A very large endothermic peak at 170 °C and a small inflection at 240 °C at 28 days show [7] the presence of cementing solids of the ettringite type having a molar ratio of $CaSO_4/Al_2O_3$ of about 2.5. The X-ray data (table 1b) shows that this phase was also present at 90 days, in addition to the low form of sulfoaluminate which was also evident from a second endothermic peak at 195 °C in a 90-day-old sample. The presence of Strätling's compound, or gehlenite hydrate, in the 7-day-old sample is also indicated by the appearance of the lines at 4.20A, 2.65A, 2.52A, and 2.42A.

The composition of the ettringite phase seems to be related to the quantity of $CaSO_4$ used (table 1c). The development of strength in the trial cements could be related qualitatively to the quantity of ettringite formed up to 28 days only, because afterwards, while there was a great increase in strength, there was no increase in the quantity of ettringite. Obviously the gain in strength at later ages is mostly due to other phases such as calcium silicate hydrate and alumina gel which may be present in amorphous or poorly crystalline state. D'Ans and Eick [8] have suggested that at a later stage in hydration some of the ettringite decomposes again to form the low sulfate compound. However, Lea [9] doubts if a change between two compounds of such different molecular volume could occur without some marked effect on the strength of the set cement. Perhaps this explains why the gain in strength from 28 to 90 days for the cement K44 was half of that for the cement K55.

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TABLE 1. *X-ray diffraction data*

a

Cement K55 (25 percent $CaSO_4$)								Cement K54 (20 percent $CaSO_4$)	
3 days		7 days		28 days		90 days		90 days	
d(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0
9.71	VVS	9.71	VVS	9.82	VWW	9.71	VVS	9.60	VVS
5.60	W	5.60	MS	5.68	VWW	5.60	WM	5.60	WM
				4.67	VVW	4.69	VVW	4.64	VVW
4.69	VWW	5.02	VW	3.91	VW	3.88	VWW	3.85	VW
3.88	VWW	4.69	VW	3.52	VW	3.49	VW	3.48	VW
3.49	W	3.88	WM	2.79	VWW	3.34	WM	3.34	VWW
3.34	VW	3.49	W	2.33	VVS	3.02	VW	2.77	VW
3.02	VW	3.34	W	2.20	VVW	2.55	VW	2.55	VWW
2.55	VW	3.02	VWW	2.02	S	2.20	VVW	2.20	VW
2.20	VW	2.86	VWW			1.82	S		
		2.55	VW						
		2.28	VVW						
		2.20	VWW						
		1.82	MS						

b

Cement K 44
(17 percent $CaSO_4$)

3 days		7 days		28 days		90 days	
d(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0
12.1	MS						
9.5	VVS	9.5	VVS	9.50	VVS	9.50	VVS
5.50	W	5.50	WM	5.60	VWW	8.85	VVW
4.65	VW						
3.85	WM	4.62	VW	4.69	VW	5.60	VWW
3.45	VWW	4.20	M	3.87	S	4.69	W
3.32	WM	3.85	WM	3.35	VVW	4.43	WW
2.54	W	3.27	VWW	2.57	VW	3.87	VW
2.15	VWW	2.65	VVW	2.20	VW	3.35	VWW
		2.52	VVW			2.84	VW
		2.42	VVW			2.70	VW
		2.28	VVW			2.57	VWW
						2.29	VVW
						2.20	VW

c

$CaSO_4$	Longest spacing at 90 days
Percent	*d*(A)
17	9.50
20	9.60
25	9.71
35	9.60

[a] Al used as an internal standard.
[b] Intensities in relation to the strongest line of Al at 2.33A.

Discussion

J. H. Welch

There are two points in Dr. Kramer's paper on which I should like to comment. The first concerns the importance of the physical state of the slag after granulation in its influence on latent hydraulicity. However efficient the granulation process adopted, a slag which is tapped at a temperature below the liquidus will already be partly crystalline and will tend to crystallize further during granulation. Providing a chemical analysis of the slag is available, a fairly reliable estimate of the liquidus temperature can be interpolated from the data of Osborn et al [16],[1] and if the slag temperature lies above the liquidus it is theoretically possible to obtain 100 percent efficiency of granulation.

The point I want to emphasize is that some years ago I demonstrated the feasibility of very rapid slag liquidus determinations by direct high-temperature microscopy, and this led to the comprehensive investigation by Baldwin [21], who used high-temperature microscopy to study slag behavior. Dr. Baldwin and I made direct comparisons of liquidus determinations on several slags both by high-temperature microscopy and standard quenching procedures, and we obtained agreement which was generally better than 5 °C. The technique is such that the liquidus of an actual slag composition can be determined without resort to chemical analysis and the use of phase diagrams within a matter of minutes. Moreover, Baldwin was able to determine the relative ease of granulation of different slag compositions and the potential crystal growth during granulation of slags which were not fully molten. He was also able to assess quantitatively the viscosity of the slags at various temperatures by direct observation of crystal movement within the melt. The viscosity-temperature relation is important in determining the probable efficiency of granulation of a particular slag composition.

The second point I wish to raise concerns the use of the factor CaO/SiO_2 ratio multiplied by the number of red-fluorescing slag particles as determined under the microscope, which has been used as an index of slag hydraulicity. Our experience at the Building Research Station of fluorescence measurements as a criterion of slag performance is that slags produced by one particular furnace or process may be usefully compared in this way, but that this does not apply to slags of varying origin. I would like to know, therefore, whether Dr. Kramer has found that the CaO/SiO_2 ratio combined with a fluorescence count can be used as a reliable index of slag behavior whatever the origin of the slag.

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[1] Figures in brackets indicate the literature references at the end of Kramer's paper, pp. 972–973.

Paper VIII–3. Portland-Pozzolan Cement*

Giovanni Malquori

Synopsis

The writer presents a general outline of the nature and trend of the results obtained by the researches that in the space of the last ten years have been carried out on pozzolanic materials and on their employment when mixed with hydrated lime or with portland cement.

In the first part, attention is paid to the differences between the peculiar constitutional characteristics of the various materials showing pozzolanic activity, and it is pointed out that in the case of the true pozzolanas the ability of their silica and alumina contents to combine with lime is principally related to the structural instability of the volcanic glass; on the other hand, for compact or semicompact volcanic tuffs—which have resulted from a transformation (autometamorphism), followed by cementation, of the incoherent products (pozzolanas) by reason of hydrothermal or pneumatolitic reactions—the above mentioned ability is to be attributed to the reactivity of the zeolitic structure.

The nature of the pozzolanic activity is next examined. The different investigational methods—differential thermal analysis, optical examination, and X-ray diffraction—when applied to investigation of the nature of the cementing compounds that result from the reaction between calcium hydroxide and the active part of the pozzolana, clearly show that these compounds are of the same type as those derived from portland-cement clinker hydration.

The determination of the activity of pozzolanas is discussed from two standpoints: the strength of mortars and concretes obtained by using as the binder the mixture hydrated lime-pozzolana or pozzolanic cement, and the ability of the pozzolanic materials to combine with lime.

Factors that increase the general resistance to corrosion are the absence of free mobile calcium hydroxide in the hardened cement, the particular texture of the latter resulting from pseudo-gelatinous bodies formed during the hardening, and their waterproofing and protective action towards more vulnerable compounds such as calcium hydroxide and aluminates.

Brief mention is made of the addition of pozzolanic materials in order to prevent expansion and cracking due to reaction between alkalies of the cement and aggregates, the heat of hydration of pozzolanic cements and its evaluation, the attempts that have been made to activate pozzolanic properties, and finally the role of pozzolanic cements in actual construction.

Résumé

L'auteur esquisse en général la nature et la tendance des résultats obtenus par les recherches qui, au cours des dix dernières années, ont été poursuivies sur les matériaux pouzzolaniques et sur leur utilisation quand on les mélange à la chaux hydratée ou au ciment portland.

Dans la première partie l'attention est attirée sur les différences entre les caractéristiques de constitution particulières des divers matériaux qui présentent une activité pouzzolanique. Il est signalé que dans le cas de pouzzolanes véritables l'aptitude de leur teneur en silice et en alumine à se combiner à la chaux est liée principalement à l'instabilité de structure du verre volcanique. D'autre part, pour les tufs volcaniques compactes ou semi-compactes—résultat d'une transformation (autométamorphisme), suivie d'une cémentation, des produits incohérents (pouzzolanes) à cause de réactions hydrothermiques ou pneumatolithiques—l'aptitude susdite doit être attribuée à la réactivité de la structure zéolitique.

La nature de l'activité pouzzolanique est ensuite examinée. Les différentes méthodes d'investigation: analyse thermique différentielle, examen optique et diffraction des rayons X, appliquées à la recherche sur la nature des composés liants qui proviennent de la réaction entre l'hydroxyde de calcium et la partie active de la pouzzolane, indiquent nettement que ces composés sont du même genre que ceux qui dérivent de l'hydratation du clinker de ciment portland.

La détermination de l'activité des pouzzolanes est discutée de deux points de vue: la résistance des mortiers et bétons obtenus en utilisant comme liant le mélange: chaux hydratée et pouzzolane ou ciment pouzzolanique, et l'aptitude des matériaux pouzzolaniques à se combiner à la chaux.

Les facteurs qui augmentent la résistance à la corrosion générale sont l'absence d'hydroxyde de calcium libre mobile dans le ciment durci, la texture particulière de ce dernier résultant de corps pseudo-gélatineux formés pendant la prise, et leur étanchéité à l'eau et leur action protectrice envers des composés plus vulnérables tels que l'hydroxyde de calcium et les aluminates.

On mentionne rapidement l'addition de matériaux pouzzolaniques pour empêcher l'expansion et la fissuration dues à la réaction entre les alcalis du ciment et des aggrégats, la chaleur d'hydratation des ciments pouzzolaniques et son évaluation, les efforts qui ont été poursuivis pour activer les propriétés pouzzolaniques, et finalement le rôle des ciments pouzzolaniques dans les constructions actuelles.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute of Industrial Chemistry, University of Naples, Italy.

Zusammenfassung

Der Verfasser gibt eine allgemeine Übersicht über die Natur und die Tendenz der Ergebnisse, die während den letzten zehn Jahren in der Pozzolanforschung gezeitigt worden sind, und er spricht auch über die Ergebnisse, die man mit Mischungen der Pozzolane mit gelöschtem Kalk oder Portlandzement erhalten hat.

Im ersten Teil werden die Verschiedenheiten zwischen den speziellen Struktureigentümlichkeiten der verschiedenen Materialien, die ein pozzolanartiges Verhalten zeigen, angedeutet, und es wird darauf hingewiesen, dass im Falle wirklicher Pozzolane die Fähigkeit der darin enthaltenden Silizium- und Aluminiumoxyde, sich mit Kalk zu verbinden, hauptsächlich durch die strukturelle Unbeständigkeit des vulkanischen Glases hervorgerufen wird. Im Gegenteil dazu muss bei den kompakten oder halbkompakten Tuffsteinen, welche durch eine Transformation (eine sogenannte Autometamorphose), mit folgender Zementation aus dem zusammenhangslosen Material (den Pozzolanen) durch hydrothermale oder pneumatolithische Reaktionen entstanden sind, die vorerwähnte Eigenschaft durch die Reaktionsfähigkeit der Zeolithstruktur hervorgerufen werden.

Im zweiten Teil wird die Natur des Pozzolanverhaltens besprochen. Die verschiedenen Methoden, wie die differentielle Thermalanalyse, die optische Betrachtung und das Röntgenbeugungsdiagramm, haben für die zementierenden Bestandteile, die durch eine Reaktion zwischen Kalziumhydroxyd und dem aktiven Teil des Pozzolans hervorgerufen werden, bewiesen, dass man es mit denselben Verbindungen zu tun hat, die auch bei der Hydratation der Portlandzementklinker entstehen.

Die Bestimmung der Pozzolanaktivität wird unter zwei Gesichtspunkten behandelt: Die Festigkeit der Mörtel und des Betons, die man erhält, wenn das Bindungsmittel gelöschter Kalk mit Pozzolan oder Pozzolanzement ist, ist ein Gesichtspunkt, und die Fähigkeit der Pozzolanmaterialien, sich mit Kalk zu verbinden, ist der andere.

Faktoren, die die allgemeine Korrosionswiderstandsfähigkeit erhöhen werden danach besprochen, namentlich, die Abwesenheit freien, beweglichen Kalziumhydroxyds im ausgehärteten Zement, die Spezialtextur eines solchen Zements, welche auf pseudogelatinöse Verbindungen zurückzuführen ist, die während des Härtens sich gebildet haben, auch ihre Wasserfestigkeit und ihr Schutz gegen den Angriff durch Kalziumhydroxyd und Aluminate.

Danach wird die Beimischung der Pozzolanmaterialien die die Ausdehnung und die Rissbildung verhindern, die als Folge der Reaktion zwischen Alkalien des Zements und der Aggregate entstehen, kurz besprochen, sowie die Erhitzung bei der Hydratation (Hydratationswärme) der Pozzolanzemente und ihre Auswertung, die Versuche, die gemacht worden sind, um Pozzolaneigenschaften zu aktivieren, und zum Schlusse die Rolle, die die Pozzolanzemente in Konstruktionsarbeiten spielen.

Introduction

The subject of this report was thoroughly treated by F. M. Lea at the Symposium on the Chemistry of Cements, held at Stockholm in 1938 [1].[1] Later, the subject of pozzolana and pozzolanic cements was widely reviewed and discussed at the Symposium on the Use of Pozzolanic Materials in Mortars and Concretes, held at San Francisco in 1949 [2], and subsequently at the Meeting for the Study and Application of Pozzolanas, organized in Rome in 1953 [3].

Moreover, a special chapter was given over to pozzolanas and pozzolanic cements in the latest edition of Lea and Desch's work, "The Chemistry of Cement and Concrete" [4]. The same subjects were also referred to in the second edition of "The Chemistry of Portland Cement" by R. H. Bogue [5].

Other publications, the original texts of which we have been unable to obtain, have appeared in recent years in the Soviet Union and in Japan, in both of which countries it has long been the practice to mix pozzolanic materials with portland cement. Indeed, the Japanese were among the first to use pozzolanic materials added to portland cement in preparing concrete for marine works, and as early as about 1930 the production of cements in the Soviet Union made increasingly large use of materials having "pozzolanic activity" when mixed with portland cement.

However, several of the problems, on which is based the interpretation of the behavior of the pozzolanic addition in cements of this type, have not yet been fully and satisfactorily cleared up, nor has decisive progress been made in this direction.

The opinion on the chemistry of pozzolanic action as a whole that R. H. Bogue expressed in his treatise is therefore still valid today: "The chemistry of pozzolanas is still not solved. . . . And only when the chemical action is completely understood will it be possible to design a 'pozzolan' of ideal composition for any particular purpose."

In the following pages we propose coordinating and setting forth briefly the data that have been obtained in recent years, to supplement those contained in the literature referred to above.

Pozzolanic Materials

The definition given by F. M. Lea [4] is quite unimpeachable: "Pozzolanas are usually defined as materials which will combine with lime at ordinary temperature, in the presence of water, to form stable insoluble compounds possessing cementing properties."

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[1] Figures in brackets indicate the literature references at the end of this paper.

The same may be said of that given by the ASTM Standard on Cement, Designation C340–58 T, which states: "Pozzolan shall be a siliceous or siliceous aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties."

Neither of the foregoing definitions makes reference to the type of material but only to its ability to combine with calcium hydroxide, in the presence of water, to form compounds possessing cementitious properties.

Pozzolanic activity therefore depends on the fixative property of the material in respect of calcium hydroxide and its ability to harden under water as a consequence of the changes the above reaction produces. These characteristics may be separate one from the other, and it may happen that while large quantities of lime are fixed by the material having pozzolanic activity the accompanying cementitious properties are quite moderate.

Materials having pozzolanic activity are therefore defined, in respect of their use, as cementitious materials, quite apart from the interpretation of the chemical and chemico-physical phenomena which are responsible for the hardening of the hydraulic binder.

There are many materials that possess this reactivity with calcium hydroxide (pozzolanic activity) and differ greatly from one another in their origin, composition, mineralogical constitution, etc. First of all, they can be divided into natural and artificial materials.

Natural Materials having Pozzolanic Activity

First place is due, for historical reasons and for their wide, well-known range of application, to the Italian volcanic pozzolanas from the Phlegraean (Pozzuoli) and the Latium (Rome) regions.

These true natural pozzolans are pyroclastic, incoherent materials that originated from prevailingly explosive types of volcanic eruption. The particles of pulverized magma entrained by the gases thus went through a strong quenching process which made them rich in glassy substance or in any case left them in a state of special instability, hence of special reactivity, also, to attack by calcium hydroxide.

The instability of volcanic glass made it vulnerable both to endogenous actions (for instance, zeolitization and cementation) and to exogenous actions (for instance, argillization).

It should be remarked that while zeolitization generally enhances pozzolanic activity, any alteration of the original volcanic glass towards the clay minerals is usually unfavorable, and indeed, diminishes this property [6, 7, 8, 9].

The intrinsic reactivity of volcanic glass in true pozzolanas is enhanced by the peculiar physical conformation of this material, because during the rapid cooling the gases originally dissolved in the liquid magma are quickly released, generating a system of small "ducts" in the solidified material and considerably increasing its surface for attack [6, 8].

The chemical composition of these pozzolanas depends on the magma from which they come. For example, the typical Phlegraean pozzolanas belong to the alkalitrachytic type, more acid, less reactive and hence less altered than the Roman pozzolanas which are instead of the leucititic type, i.e., more basic.

B. Tavasci [10, 11] examined several samples of Latian and Phlegraean pozzolanas under the microscope, observing that while the Segni pozzolana—which belongs to the Latian leucititic type—consists essentially of leucite dendrites and some parts of augite, cemented by a groundmass of considerably altered glass, the Bacoli pozzolana (Phlegraean) is, instead, made essentially of bubbled glass, with a few inclusions of sanidine crystals, and still more seldom of plagioclases and pyroxenes [12].

Tavasci [10] appears, moreover, to have noted the presence of zeolites in the Latian pozzolana, that is, of the crystalline formations that can be classified as of the chabazite and phillipsite group.

Nothing of this kind has been observed by other experimentalists in the Phlegraean pozzolanas [13] which, as already stated, appear far less altered than the Latian ones.

Besides the Latian and Phlegraean pozzolanas mentioned above, other volcanic regions of the Italian peninsula supply natural pozzolanas. No true pozzolanas are found in the volcanic system of Mount Etna (Catania), but only volcanic ashes, incoherent, mainly crystalline, and very little altered, owing to the lack of prevailingly explosive eruptions. The volcanic ashes thrown out by Vesuvius subsequent to the explosive type of eruption described by Pliny the Younger are also mostly crystalline (leucotephritic), hence with little or no pozzolanic activity.

Ashes and lavas of identical mineralogical composition, originating from alkalitrachytic, leucititic, leucotephritic and haüynophyric types of magma, forced to solidify as a glass by melting and subsequent quenching, acquire pozzolanic properties.

The glass obtained is highly reactive towards calcium hydroxide solution.

Volcanic, pyroclastic, incoherent materials with pozzolanic properties have been reported in various parts of the world, and some of them, like Santorin Earth (Grecian isle of Santorin), have been widely used for practical purposes.

In conclusion it can be stated that the action of true natural pozzolanas is determined by the type of original magma, and principally the origin and history of the pyroclastic material, on which depends the quantity of glassy fraction and its extent of alteration. Metamorphic or diagenetic alterations may have a favorable or unfavorable influence on the material's pozzolanic activity.

Compact volcanic tuffs, which are used in the pulverized state as pozzolanic material, are quite different from the true natural pozzolanas described above. They originate from the same pyroclastic materials but involve a transformation process.

The best known example is the Rhenish "trass," obtained by grinding the very soft tufaceous rock from the Eifel quarries, and especially from those in the Nette and Brohl valleys, close to Neuwied and Andernach.

The original tufaceous rock is found together with an incoherent, mainly pumice-like material, likewise of volcanic origin. An intervening stratum of weakly coherent material divides the compact tuff from the incoherent pyroclastic material mentioned above.

The beds therefore lie in a very similar way to those of Neapolitan yellow tuff [9] which is constitutionally similar to the Rhenish volcanic tuff [14, 15]. Both are of the alkalitrachytic type, with almost the same chemical composition, and thin sections viewed under the microscope present an apparently isotropic groundmass, incorporating fragments of pumices and crystals of the minerals found in the original pyroclastic materials: sanidine, augite, hornblende, biotite, etc.

The cementing groundmass appears markedly altered; it is essentially zeolitic, its main constituent being herschelite, which comes from the alteration (autometamorphism) of the glass in the original pyroclastic materials owing to hydrothermal or pneumatolytic action.

The zeolitization of artificial obsidians (glasses) of the rhyolitic, alkalitrachytic [16], leucititic, leucotephritic [17], haüynophyric [18], and basaltic [19] types has been reproduced in the laboratories of the Institute of Industrial Chemistry, University of Naples. It has thus been possible to reproduce some examples of compact volcanic tuff starting from natural, essentially glassy pyroclastic materials, such as the Phlegraean pozzolanas [9], and in this way to throw light on the origin of these tuffs which, as already mentioned, is assumed to lie in the alteration occurring in volcanic glass as a result of hydrothermal or pneumatolytic action.

Like the Rhenish "trass," the Neapolitan yellow tuff, when pulverized, reveals considerable pozzolanic activity, both in fixing calcium hydroxide and in its general behavior when mixed with portland cement to produce pozzolanic cement.

Constitutional characteristics very closely similar to those of Neapolitan yellow tuff and Rhenish tuff from the Eifel district are to be found in an alkalitrachytic, light yellow, compact tuff from the Grand Canary, recently examined by us [20]. In the apparently isotropic groundmass, which cements inclusions of various types among which sanidine crystals and pumices predominate, phillipsite can be detected.

The tuffs from the Latian volcanic region, of the leucititic type, are highly zeolitized, and the zeolites that we were able to find both as cementing groundmass constituents and as well-formed crystals lining the cavities in the material were: chabazite, phillipsite and herschelite [21, 22, 23].

Comments on the presence of zeolites in the cementing groundmass of volcanic tuffs are given in the literature [24, 25, 26, 27].

Altered rhyolitic volcanic tuffs, no longer containing glass because they are deeply zeolitized to clinoptilolite (high-calcium heulandite) and to analcite, have been mentioned by R. C. Mielenz, L. P. Witte, and O. J. Glantz as having pozzolanic activity [28].

Tufaceous compact rocks which can be ground to produce "trass" have been reported and utilized in other parts of the world—for instance, in Bavaria, Rumania [29], and Crimea.

Evidently there exists between the true pozzolanas, incoherent and rich in glass component, and the compact tuffs which originated from the cementation of pyroclastic materials, a series with intermediate characteristics according to the type and extent of alteration that has occurred. All these materials possess varying degrees of pozzolanic activity.

In the tuffs mentioned, the alteration (autometamorphism) of the original natural glass by hydrothermal or pneumatolytic action, which induced cementation of the pyroclastic, incoherent, original material, caused zeolitization. Consequent upon this change the final product, i.e., the tuff, was found in our research to be more reactive to calcium hydroxide than was the starting material (pozzolana).

In the light of the foregoing, true pozzolanas can be distinguished from "trass," as there is a fundamental constitutional difference between these two materials both possessing pozzolanic properties. The term "trass" therefore should be applied only to the product obtained by grinding tufaceous rocks formed by zeolitization of the glassy portion of primary pyroclastic materials.

It is known that the water stably retained by the material when dried at 100–105 °C is considered as a quality indication for "trass" [30]. This factor is actually indicative of its degree of zeolitization. The water in question is given up in a regular way by heating at rising temperatures.

That this difference has not been elucidated explains why some researchers have found that the true pozzolanas, Latian and Phlegraean, have only a very weak [25, 31] aptitude for base-exchange, whereas this is appreciable in "trass" and volcanic tuffs constitutionally similar thereto, precisely because of their characteristic degree of zeolitization.

Besides the true, incoherent pozzolanas, the pumices, and compact volcanic tuffs, several other natural materials have pozzolanic activity. Examples are lavas containing a fair percent of glassy component; products of various kinds deriving from extensive alteration of different types of volcanic rock by numerous causes; opaline silica; diatomaceous earths; clays which have been naturally roasted by incandescent lava flowing over them, etc.

Among others may be mentioned the Danish "moler," the French "gaize," the "tripel" from Briansk, consisting of amorphous silica which, in conjunction with another material already mentioned—liparitic tuff from Karadagh (Crimea)—is used in the Soviet Union for making pozzolanic cement.

Artificial Material Showing Pozzolanic Activity

First place must today be given to "fly ash," a residue from the combustion of solid pulverized fuels in big thermoelectric power plants. Its essentially vitreous physical state, provided it is accompanied by an appropriate composition and admissible content of unburnt carbon matter, suits it for use in pozzolanic materials, and Europe is following the example of the United States in extending its use for this purpose.

Fly ash usually has a low alkali content, because of its origin, lower than that of the true Italian pozzolanas and the volcanic tuffs employed for their pozzolanic properties ("trass").

Next in importance are the roasted clays, which are dehydrated at suitable temperature, this varying according to the type of silico-aluminous constituents (kaolinite, montmorillonite, illite groups). Heat treatment endows the clay with pozzolanic properties in that, apart from any interpretation as to the nature of the change induced by dehydration, the elimination of water brings out silica and alumina which readily react with calcium hydroxide in the presence of water·

Other natural materials that are activated by heat treatment are the "moler" and "gaize" already referred to. Dehydration essentially activates the clay fraction that they originally contain. There are also some entirely artificial materials, consisting of certain waste matters from the chemical industry, for instance: "Si-stoff." These, however, have a narrow range of use and are therefore not of general interest.

Blast-furnace slags cannot be classified as pozzolanic materials since they differ from these both in composition and in the manner of their hydraulic action.

Actually, while the pozzolanas, irrespective of their origin and composition, turn into compounds with cementitious properties only through fixation of calcium hydroxide, granulated blast-furnace slags, i.e., glassy slags, with hydraulic properties, are in themselves sufficiently basic and therefore have but a weak pozzolanic activity, in the sense of their ability to combine with lime coming from the saturated contact solution.

Pozzolanic Activity

The materials referred to in the previous section are of widely differing types according to their origin, composition, constitution and structure. But all possess, according to the definition, the property of reacting with calcium hydroxide in the presence of water to form compounds possessing cementitious properties; which will presumably be the same, or very similar, irrespective of the initial system, i.e., of the type of pozzolanic material made to react with lime.

In appraising the pozzolanic activity of any given material, in the sense of its ability to combine with lime, account must be taken of the chemical components, of their chemical bonds, and of the physical state.

Silica and alumina are, in effect, vulnerable to calcium hydroxide when their structural bonds are weak and unstable in the original material, as is the case with volcanic glass, or the zeolitic structure deriving from the alteration thereof. The same applies to clay materials when, through total dehydration by heat treatment, the bonds between silica and alumina are relaxed or annihilated.

If, instead, Si, Al, and O are bound in the lattices of the individual minerals formed by crystallization of the magma, or in those of the silico-aluminous materials which constitute natural clays, the calcium hydroxide acts far more slowly or not at all.

From the standpoint of cementitious action, that is, the hardening process, the parts played by silica and alumina cannot be considered separate one from the other. It has already been said that there are siliceous materials with no, or very little, alumina, which while rapidly fixing noteworthy quantities of calcium hydroxide from its saturated solution, do not offer such a satisfactory performance from the standpoint of hardening, and produce low mechanical resistance when mixed with lime to make mortars and concretes.

According to F. Murakami [32] the presence of reactive alumina considerably enhances the mechanical strength of pozzolanic cements, particularly for brief curing.

Practically nothing has yet been learned of the part played by the minor components of pozzolanic materials, i.e., iron and alkalis. It may be assumed that when the original structural arrangement of the starting material is destroyed by the attack of calcium hydroxide, the iron undergoes changes similar to those occurring in alumina though far slower and that the alkali remains partly fixed by the newly formed pseudogelatinous products. There should not, however, be a very appreciable effect on the final arrangement of the final system.

The results of our investigations have shown [14, 33] that the zeolitic structures that we found in the volcanic tuffs examined—chabazite, herschelite, and phillipsite—are attacked more quickly by calcium hydroxide than are the true, practically entirely glassy pozzolanas, the cementation of which produced these tuffs.

Both the zeolitized tuffs and the single zeolites tested in a constantly saturated solution of calcium hydroxide revealed a strong capacity for fixation, considerably higher than that corresponding to a mere base exchange [34]. At the same time, the performance of these materials from the standpoint of cementitious properties was good [35].

This observation confirms what F. M. Lea [1, 3] has asserted for some time, that the pozzolanic activity of "trass" is not correlated with its ability for base exchange.

The single zeolites and zeolitized tuffs that we examined revealed a normal base-exchange capacity, more or less in the ratio of the equivalents, but the quantity of calcium hydroxide involved in the mere base exchange is far smaller than that fixed by the material kept in contact with a constantly saturated solution of calcium hydroxide. The calcium hydroxide does not, therefore, act on the zeolitized material merely by base exchange with the alkalis, but by breaking down the zeolitic structure, after which the silica and alumina are enabled to combine with the calcium hydroxide to form cementitious compounds.

In other words, the quantities of calcium hydroxide involved in an ion-exchange process are small and do not explain the far-reaching radical change that is responsible for the hardening of the material when it is mixed with hydrated lime to form mortars and concretes.

It is the zeolitic structure and its instability that make the zeolitized material more highly reactive to calcium hydroxide than are the eminently glassy pozzolanas.

In handling the question of the chemistry of pozzolanic cements it is obviously necessary to interpret and elucidate all aspects of the phenomena which play a part in the hydraulic action of materials having a pozzolanic effect, whatever their origins and composition may be.

Unfortunately no final elucidation has yet been forthcoming on the series of changes through which these materials perform their role of hydraulic binders. The main reason lies in the difficulties of testing and interpreting the very nature of these systems, which make it extremely arduous, not to say impossible, to distinguish real from apparent equilibrium, stable from transient arrangements.

Once having identified, in the reaction between calcium hydroxide and materials with pozzolanic activity, the chemical phenomenon responsible for their hydraulic behavior, it was obvious that one might attempt to throw further light thereon not only by studying the nature of the reaction solids with a view to identifying the final, stable structure of the system, but also by studying the evolution towards the hypothethical condition of stability.

One calls it hypothetical, because diagnosis is a difficult and complex task. The pozzolana grain is attacked from outside and is gradually coated with newly formed products which protect the kernel in a manner that prevents any estimation or time-wise evaluation of the products originating from the calcium hydroxide attack on the pozzolanic material.

However, apart from an interpretation of the process by which calcium hydroxide attacks material, at the outset of our investigations we concerned ourselves with two aspects which we considered of interest: the extent and the velocity of fixation of calcium hydroxide by pozzolanic materials kept in contact with constantly saturated solutions [7].

The extent varies according to the type of pozzolanic material in question, its composition, constitution, and content of minerals weakly, or not at all, susceptible to attack. The velocity is perhaps the most useful indication; for if it is true that the various pozzolanas, mixed with hydrated line or portland cement and tested in mortar or concrete, reveal little difference in strength over long periods of wet storage, there is a definite difference over short periods.

At all events, an interpretation of pozzolanic activity as a whole cannot be given only on the basis of these two characteristics. There is a third far more complex aspect which concerns the nature of the transformations, i.e., the chemical and physical phenomena that occur as a result of the attack by the lime.

It has been stated, in principle, that materials with a high reactive silica content will, if kept constantly in contact with a saturated solution, speedily bind large quantities of calcium hydroxide, yet when used in mortar or concrete they reveal mechanical strength decidedly below that obtained when using true natural pozzolanas in the very same way, although the latter give a less satisfactory response [36] from the standpoint of the characteristics referred to above, particularly velocity.

Quite some time ago we developed a very simple method for testing the ability of pozzolanic material to combine with lime, which furnished a sufficiently close evaluation [7, 36]. The test, currently in use, consists of adding separately greater and greater amounts of CaO to equal quantities of the pozzolanic material that is being tested, which is ground to a given fineness and placed in sealed bottles, with a constant volume of water free from CO_2. The bottles are continually agitated, and the lime content of the contact solution is determined at regular intervals, as well as the amount of alkalis that may be given up by the pozzolanic material as the lime attack proceeds, until the percent of CaO (gravimetric) drops and remains below that of the saturated solution at the test temperature and for the alkali content that is separately determined. The alkali is inferred from measuring the solution alkalinity or by direct spectrophotometric assay [37].

This procedure gives the time required for a given weight of material tested to fix an amount of lime equal to the weight of CaO present in the system on commencement of the test, less the amount removed with the single titrations and the lime still in solution in the residual liquid. The different times taken for fixation of the varying quantities of CaO made to react with the initial system enables one to draw the curves showing the speed of attack.

There is every reason to assume that, at the end of the transformation that they undergo by the action of lime, pozzolanic materials must have produced cementitious compounds that are probably of the same type as those constituting the final system obtained by hydration of the anhydrous components of portland cement clinker.

In the case of materials with pozzolanic activity, which must combine with lime to reach conditions of stability in the Al_2O_3–SiO_2–CaO–H_2O system (ignoring the minor components), the course of the transformation must perforce differ from those occurring in the hydration of clinker, and it is not easy to follow this, mainly because of the difficulty in distinguishing transient from permanent arrangements.

The test referred to has shown that pozzolanas are, at ordinary temperature, able to fix large amounts of calcium hydroxide from constantly saturated solutions; and that these amounts are greater by far than those ascertainable using the various modifications of Vicat's test, the results of which lead to a wrong evaluation of pozzolana lime-retaining capacity.

In investigating the effect of lime on both Latian and Phlegraean pozzolanas, we found [38] by X-ray examination that materials that had fixed between 40 and 70 g of CaO per 100 g of pozzolana—by contact with constantly saturated calcium hydroxide solution—showed quite distinguishable lines characteristic of the solids in the SiO_2–CaO–H_2O system for CaO-SiO_2 ratios between 1 and 1.5; and that when observed in transmitted light through the microscope they revealed a nonresolvable, amorphous groundmass embodying thin, hexagonal contour lamellae very similar in appearance to the hexagonal crystals of calcium aluminate hydrates and to the lamellae perceivable among the products of the reaction between calcium hydroxide solution and dehydrated kaolin.

It was not possible to obtain any evidence of the presence of Strätling's compound, C_2SAH_x in the groundmass.

Attempts to follow the development of the solid in contact with the constantly saturated lime solution by means of chemical attack of various kinds were unsuccessful, nor was any type of fractionation efficient or suitable for the purpose.

Later, R. Turriziani was able, with more efficient experimental facilities [39] to improve the first investigations referred to above, and using differential thermal analysis and X-ray methods he studied the solids that form when Segni pozzolana (Latium, leucititic type) remains for a long time in contact with a constantly saturated lime solution. He remarked that the differential-thermal-analysis (DTA) curves revealed a first endothermic effect at low temperature (140 °C) which can be ascribed to the presence of Taylor's silicate: $C_{0.8-1.5}SH(I)$, and a second effect (220 °C) which can be attributed to the presence of C_4AH_{13}. This finding was corroborated by the X-ray diffraction data. Nevertheless, the presence of small quantities of C_2SAH_x cannot definitely be ruled out.

In addition, R. Turriziani [40] examined the products of the reaction of Segni pozzolana and calcium hydroxide mixed in varying proportions (the tests being performed in a different manner from that indicated above—that is, by keeping the mixtures in a fluid state up to the end of the investigations) and also true mortars prepared with currently employed proportions and kept in water. The DTA and X-ray examination of the solids confirmed the presence of calcium silicate of tobermoritic type. Alumina is found in the mortars in the form of C_4AH_{13}; in other preparations the compounds C_2SAH_x prevails instead.

According to J. Chapelle [41] the action of lime on materials having pozzolanic properties produces calcium silicate CSH_x and tetracalcium aluminate C_4AH_x. The latter transforms to cubic C_3AH_6 if the reaction between pozzolana and saturated lime solution takes place at the boiling point. This researcher was unable to identify silico-aluminate, C_2SAH_x.

The reaction between pozzolana and calcium hydroxide has also been studied by R. Turriziani, at a temperature of 45 °C [40]. This study confirmed the presence of C_3AH_6 (cubic) already reported by G. Malquori and V. Cirilli [38] in the solids of the dehydrated kaolin-lime-water system at a temperature of 70–80 °C.

Kaolin dehydrated at between 600 °C and 700 °C, if kept at ordinary temperature in contact with a constantly saturated calcium hydroxide solution, will fix considerable quantities, tending to a saturation point represented by the ratio $3CaO{:}2SiO_2 \cdot Al_2O_3$ [38].

In following the development of the groundmass under the microscope it was possible to note, embodied in a mass consisting partly of nonresolvable material and partly of small birefringent scales, hexagonally contoured laminae, looking very much like those of the hexagonally shaped calcium aluminate scales, but with a slightly lower refractive index than the latter.

On heating the solids at 70–80 °C in the presence of their equilibrium solution, crystals of the cubic system were seen to appear (trapezohedra, hexakisoctahedra), outwardly similar to cubic aluminate C_3AH_6 crystals. At the same time it was found that the above change is greater in velocity and intensity the higher the CaO content of the solution.

In X-ray diffraction patterns of the various groundmasses having different CaO contents and obtained by keeping the system at ordinary temperature, besides the lines characteristic of the solids of the SiO_2–CaO–H_2O system, for CaO/SiO_2 ratios between 1.5 and 1 there appeared new lines that did not belong to the patterns of any of the calcium aluminate hydrates. The diffraction patterns were like those obtained by Strätling and ascribed by him to the compound C_2SAH_x [42, 43].

The presence of the tobermoritic type of calcium silicate, as well as of C_2SAH_x, was confirmed by R. Turriziani and G. Schippa [44] by means of X-ray investigation and DTA.

V. Cirilli [45] saturated kaolin, dehydrated at 630–700 °C, with lime, by contact with a constantly saturated calcium hydroxide solution. Subsequently he processed the solid thus obtained by progressive hydrolysis, the course of which appears to rule out the presence of free calcium aluminates.

Likewise, according to R. Turriziani and G. Schippa [46], the solid cubic phase containing alumina, found among the products of reaction of calcium hydroxide and dehydrated kaolin in the presence of water at 50 °C, appears to be a hydrogarnet of the C_3AH_6–C_3S_3A series containing 0.3 to 0.4 molecules of silica.

Results obtained by observing lime-pozzolana motars under the microscope are no more promising.

G. Gallo [47] had formerly examined mortars consisting of three parts (by volume) of pozzolana to one of hydrated lime, and in the nonresolvable, amorphous groundmass of the newly formed products had identified hexagonal crystals which he ascribed to the aluminate C_3AH_{10}.

Later, B. Tavasci [11, 48, 49], examined both thin sections and polished sections of lime-pozzolana mortars, cured in water for about five years, and having a lower lime content than the above specimens. Among the newly formed products he was able to identify lamellar crystals whose appearance and optical characteristics led him to classify them as calcium aluminate hydrates.

The groundmass is isotropic and when magnified appears to have a granular structure. It was impossible to establish its nature merely by optical examination; however, while the possible presence of C_2SAH_x cannot be excluded, it is probable that the principal component of the mass is a low-lime silicate hydrate of the okenite type CS_2H_2.

On the whole, the optical investigations carried out by numerous researchers on the solids resulting from reaction of pozzolana with calcium hydroxide, and on pozzolana mortars, have not produced more than approximate data on the nature of the solids that are formed by this reaction.

The identification of newly formed solids, viz, of the cementitious compounds present in the materials examined, has been greatly aided by DTA and roentgenographic techniques which, while not in themselves decisive, are reciprocally complementary and, considered in conjunction with optical findings, contribute to the final diagnosis, which may be summarized as follows:

(a) The presence of calcium silicate hydrate of the tobermoritic type has been ascertained as an apparently amorphous groundmass, in the form of a gel and in any case having a low degree of crystallization.

Since the tobermorite highest in lime is stable in a calcium hydroxide solution having a near-saturation titer, while the lower-lime forms are stable in weaker solutions (0.28 g/liter of CaO), the composition of the calcium silicate hydrate in hardened pozzolana mortars, although remaining within the tobermorite range, must vary.

In hardened high-pozzolana mortars, the tobermorite present should correspond to the low-lime form.

(b) The presence of calcium aluminate hydrate, probably C_4AH_{13}, was ascertained.

(c) The presence of C_2SAH_x was not sufficiently established.

The whole collective data seem to warrant the opinion that the cementitious compounds formed by pozzolanic action are of the same type as those formed by hydration of portland cement.

Material having pozzolanic activity, if kept in contact with a constantly saturated calcium hydroxide solution, is more quickly attacked if calcium sulfate is present at the same time.

Likewise, if calcium hydroxide is added to the pozzolana-calcium sulfate-water system (the solution being always saturated with $CaSO_4 \cdot 2H_2O$), the lime is fixed by the pozzolana far more quickly than when calcium sulfate is absent [50].

This behavior is characteristic of materials containing alumina, and not only of pozzolanic materials. By sulfo-calcic attack alumina can be made to react in minerals that at ordinary temperature withstand attack by calcium hydroxide alone [50].

G. Malquori and A. Spadano [50] noted furthermore that when pozzolanic materials are attacked by calcium sulfate in the presence of excess quantities of calcium hydroxide, the solid swells markedly, and in direct proportion to the quantity of sulfate retained by the material.

Observation under the microscope has in each case revealed the characteristic needle-shaped crystals of the high-sulfate form of calcium sulfoaluminate: $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

The results summarized in the foregoing proved that sulfo-calcic attack was more vigorous than attack by calcium hydroxide alone, that the alumina in the pozzolana was quickly and entirely attacked by the combined action of calcium hydroxide and sulfate, and that in every case the high-sulfate sulfoaluminate was formed.

More recently R. Turriziani and G. Schippa [51, 52] studied the behavior of mixtures of pozzolana, hydrated lime, gypsum, and water using various proportions, and employing DTA and X-ray techniques in their investigations. They obtained evidence of the presence of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ and, under certain conditions, of $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$. They rule out all possibility of C_2ASH_x being present at the same time.

J. Chapelle [41] supports the previous findings of G. Malquori and A. Spadano on the behavior of pozzolanic materials containing alumina in connection with the combined action of calcium hydroxide and sulfate, and confirms that the alumina is exclusively taken up in the sulfoaluminate.

To corroborate the foregoing observations on the vulnerability of the alumina contained in pozzolanic materials when attacked by calcium sulfate, F. Parissi [53] and G. Malquori and F. Sasso [54] had shown that pozzolanic cements prepared with Italian pozzolanas—which are silico-aluminous—do not withstand the Anstett test, especially if this is performed after short periods of water curing; moreover, if gypsum is added to the hydrated lime-pozzolana (silico-aluminous) mortar this causes marked expansion, approximately proportional to the percent of gypsum added to the initial mixture (for the same ratio of pozzolana to hydrated lime).

The swelling is so marked as to crack the test specimens, and occurs all the more rapidly the higher the percent of gypsum initially present. The compressive strength of test specimens of mortar prepared from the ternary mixtures likewise drops quickly when the proportion of gypsum is increased. The expansion of the test specimens is always accompanied by the formation of high-sulfate sulfoaluminate.

R. Turriziani and G. Schippa [40, 51, 52], also investigated the compressive strength of mortars obtained by mixing Latian pozzolana, hydrated lime and varying quantities of gypsum, and found a slight increase in strength up to 6 percent of gypsum added. Above 10 percent, however, with even short periods of storage, the test specimens became swollen and disintegrated, hence more or less without mechanical strength.

These researchers also believe that the decrease in mechanical strength noted in their pozzolanic-mortar test specimens is due to the formation of expansive sulfoaluminate, which takes place more quickly than fixation of lime by the pozzolana [50].

There is every reason to assume that the change occurring in pozzolana when it is mixed with hydrated lime to form pozzolanic mortar proceeds more or less in the same way as in the case of mixtures of pozzolana and portland cement.

R. Turriziani [40] recently succeeded in corroborating this assumption by examining portland cement and pozzolanic cement pastes made by mixing the former with Italian pozzolana (Segni). The pastes were wet cured at 18 °C for one year, and throughout the transformation of the material to its final arrangement, followed over a period of one year, samples were taken at given intervals, appropriately conditioned and examined by DTA and roentgenographic methods. In the portland-cement pastes it was possible to identify calcium silicate hydrate of the tobermoritic type, tetracalcium aluminate hydrate, free calcium hydroxide resulting from hydrolysis, and high-sulfate sulfoaluminate. Neither the compound C_2ASH_x nor low-sulfate sulfoaluminate could be identified. With pozzolanic cement, the components of the hardened pastes appear the same. However, as was to be expected, the calcium hydroxide content was markedly less (fig. 1).

B. Tavasci [55] examined hardened pastes of both portland and pozzolanic cements under the microscope, observing that the pozzolanic cement-paste structure seems intermediate between that of portland cement and of hydrated lime-pozzolana mortars. In pozzolanic cement pastes the free calcium hydroxide produced by hydrolysis of the clinker constituents is still visible, although obviously considerably less than in portland-cement pastes. B. Tavasci remarks that the larger pozzolana granules appear strongly attacked and surrounded by a thick layer of newly formed products.

R. Turriziani and A. Rio [56] attempted to determine the free calcium hydroxide present in pozzolanic cement pastes wet-cured for different lengths of time; they made use both of Franke's solubilization method and DTA, and concluded that apart from quantitative accuracy it was an ascertained fact that the hardened pozzolanic cement pastes examined, even those prepared with a high pozzolana content and given the longest wet-curing, always contained free calcium hydroxide produced by hydrolysis of the clinker constituents, although to a much smaller extent than observed in portland-cement pastes.

Altogether the foregoing considerations prove that pozzolanic cements are potentially susceptible to attack by aggressive agents.

Little is known of the behavior of the minor constituents in the hardening process of mortars of hydrated lime and pozzolana and of pozzolanic cements.

For Fe_2O_3 the methods of research employed so far have not succeeded in distinguishing the ternary combinations $CaO–Fe_2O_3–H_2O$ from the corresponding ones containing alumina. The diffraction pattern of tetracalcium ferrite hydrate is similar to that of tetracalcium aluminate hydrate, at least in the zone of the more intense lines, and the same thing is true of the complex salts with the sulfuric radical. However, bearing in mind that the gel of ferric hydroxide fixes calcium hydroxide only very slowly, it must be concluded that even assuming part of the ferric oxide contained in the pozzolana to be reactive, it can play but a minor part in the fixation of the lime and in the setting and hardening process.

The classical natural pozzolanas, for instance the Italian leucititic and alkalitrachytic pozzolanas, contain noteworthy percentages of alkalis which are freed during the transformation caused by lime attack. A. Rio, for example [57], has tested pozzolanic cement pastes, made with the same clinker and varying percentages of Segni and of Bacoli pozzolanas, at different periods of cur-

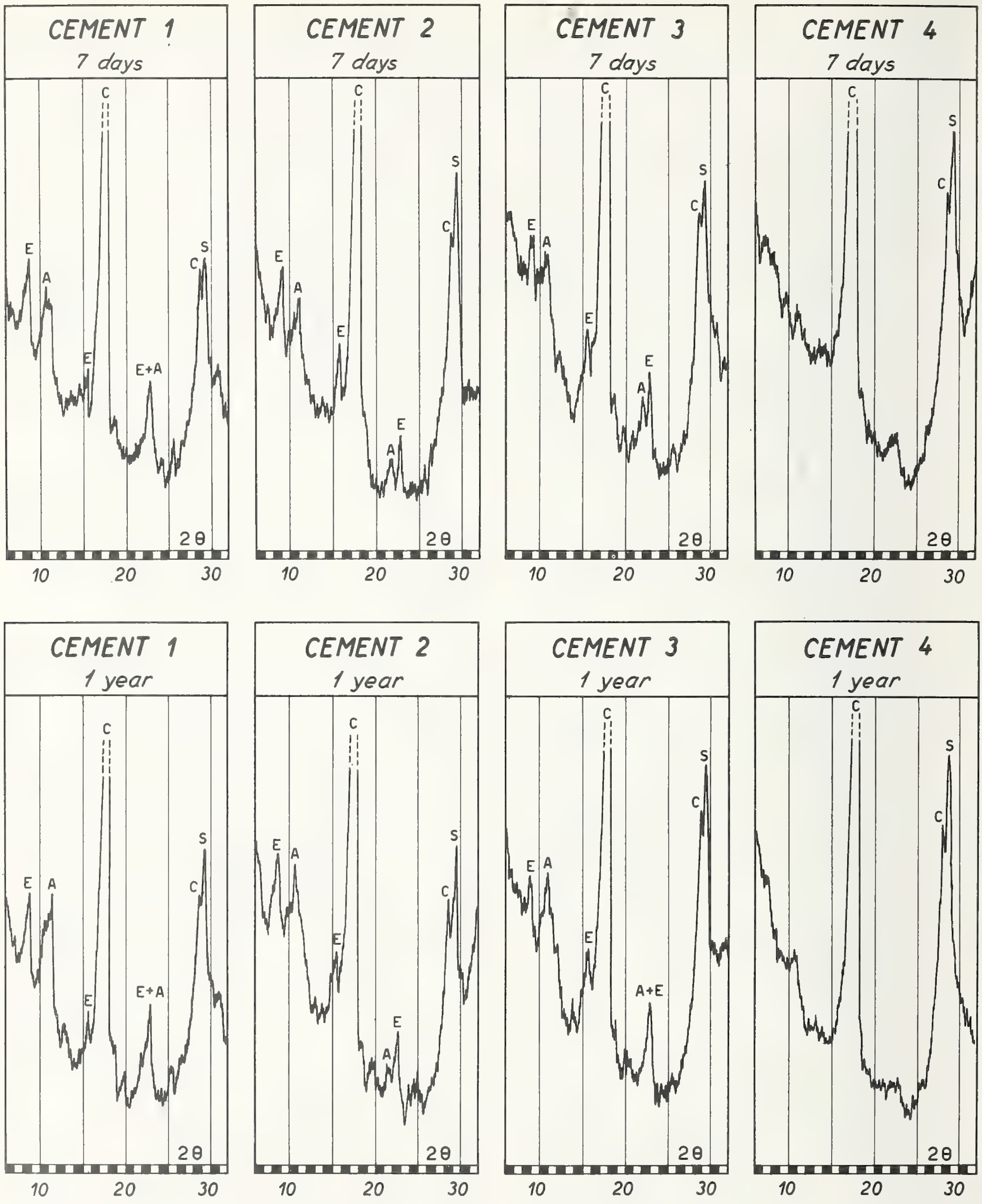

FIGURE 1a. *X-ray diffractograms of portland cement pastes.*

w/c=0.30; E=ettringite; A=tetracalcium aluminate; C=calcium hydroxide; S=calcium silicate. From R. Turriziani [40].

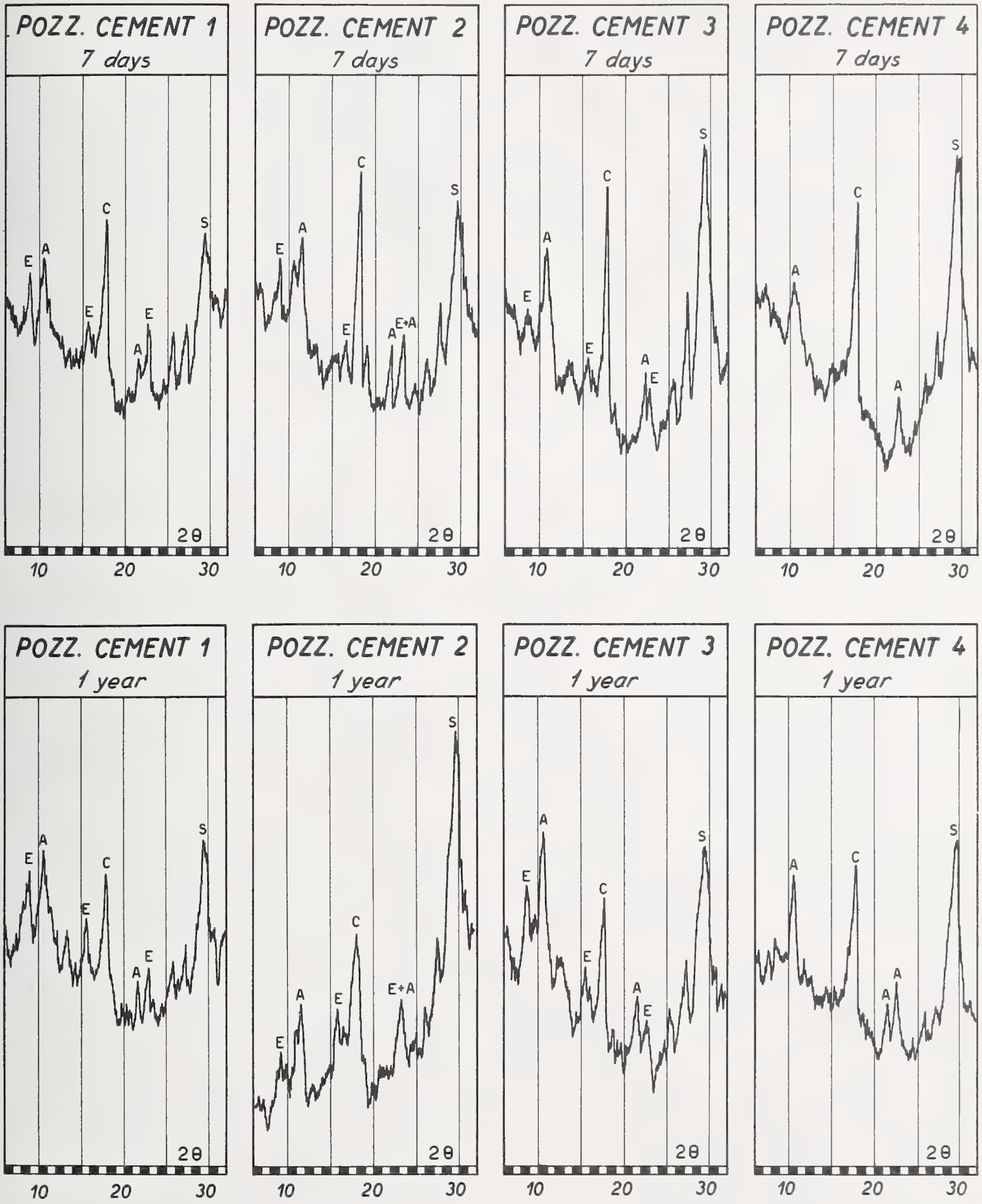

FIGURE 1b. *X-ray diffractograms of portland-pozzolan cement pastes.*

w/c=0.35; E=ettringite; A=tetracalcium aluminate; C=calcium hydroxide; S=calcium silicate. From R. Turriziani [40].

ing, and found that after one year the Segni pozzolana gave up 85 percent of its initial alkali content, and the Bacoli pozzolana 55 percent.

Alkalies not only decrease calcium hydroxide solubility, but probably become fixed on the pseudogelatinous newly formed compounds.

Unfortunately very little is known about the systems SiO_2–Al_2O_3–CaO–K_2O–H_2O and SiO_2–Al_2O_3–CaO–Na_2O–H_2O, and it is hoped that in the near future these fields will be appropriately investigated. It should be repeated, nevertheless, that the research so far carried out on the constituents of hydrated lime and pozzolana mortars and on hardened pozzolanic cements, has shown that the products of the reaction between calcium hydroxide and silica and reactive alumina in the pozzolana, are the same as those indicated when hardened portland cements are investigated in the same way.

It is therefore a justifiable conclusion that the presence of alkali has no substantial influence either on the way in which the transformation proceeds or on the nature of the end products, except, perhaps, from the standpoint of kinetics, considering that, among other things, the solubility of calcium hydroxide drops.

Evaluation of the Pozzolanic Activity

According to the definition, the constituents of pozzolanic material must have the ability to combine with calcium hydroxide to form compounds possessing cementitious properties.

It is evidently desirable for this action to take place as rapidly and intensely as possible.

There are as yet no sufficiently reliable tests for predicting *a priori* how pozzolanic material mixed with hydrated lime or portland cement in mortar or concrete will behave, either from the standpoint of mechanical-strength performance or from that of reduction of free calcium hydroxide in the hardened binder. Nor does ability to fix calcium hydroxide from a constantly saturated solution arrange the different materials according to the order in which they are rated if tested in mortars or in concrete in association with hydrated lime or portland cement.

Reactivity tests, viz, solubilization by chemical acid-basic attack of both the original pozzolanic material and the same material after reaction with lime, have proved equally unsatisfactory.

It thus follows that an evaluation of pozzolanic material for purposes of its addition to portland cement must be based on two factors: the mechanical strength of mortars and concretes made up with a portland-pozzolana mixture, and the disappearance, or anyway the reduction, of free calcium hydroxide in the hardened pozzolanic cement.

These two factors must be considered and rated separately, observing the behavior of the mortar or concrete under conditions that are as nearly as possible those of current practice.

This requirement means determining under standard conditions both the mechanical strength of the mortars or concretes [58, 59] and the extent to which free calcium hydroxide is reduced, or the characteristics of the mixture (mortar and concrete) that are correlated with the lack or scarcity of free calcium hydroxide.

These tests must be designed with a view to their practical purpose, hence speed is required when the test is proposed for acceptance or rejection of pozzolanic material.

With regard to mechanical strength, especially that of hydrated lime-pozzolan mortars, it was suggested long ago that the hardening time be speeded up by curing the test specimens at higher than normal temperature. The ASTM C340–58T test, for instance, specifies curing the test specimens at 55 ± 1.7 °C.

An evaluation of the second factor in pozzolanic activity, namely, the material's ability to combine with calcium hydroxide, based on determination of the free calcium hydroxide in the pastes, mortars, or concretes after reasonably short periods of curing, is inaccurate, whether this test is performed by dissolving or by extraction with chemical reagents, or whether DTA and thermogravimetric analysis are used. Not only that, but in this evaluation it must be borne in mind that when pozzolanic binders harden, a portion of the calcium hydroxide remains embodied and protected by the newly formed pseudogelatinous products, which impede its passage into solution. This immobilized calcium hydroxide will be again found to a great extent as free hydroxide in the pulverized material which is tested as mentioned above.

N. Fratini [60], for instance, found that one week after preparation a portland-cement paste gives up so much calcium hydroxide during wet curing that it saturates the contact solution. But he found that this is not the case with a pozzolanic cement paste made from a mixture of portland cement and Italian pozzolana in the ratio: $\frac{SiO_2+R_2O_3}{CaO} \geq 1$, despite the fact that the mass, i.e., the cement paste, contains free calcium hydroxide identifiable both with solubilizing reagents and with DTA.

This behavior corroborates the suggestion advanced that part of the calcium hydroxide released by hydrolysis of the clinker constituents is enclosed, protected and thus immobilized. It would seem that protective films of newly formed products passivate the crystals.

N. Fratini [61] also proposed an accelerated test [62, 63, 64], for determining, apart from the composition ratio: $\frac{SiO_2+R_2O_3}{CaO}$, or the portland-pozzolana ratio of the mixture, whether a cement claimed to be "pozzolanic" will not, when tested in paste form by standard methods, give up enough calcium hydroxide to the contact solution to saturate it. The method consists of determining the total alkalinity and the calcium hydroxide content of the solution in which the tested paste is steeped during curing under predetermined conditions. Having ascertained the solubility of calcium hydroxide in the presence of alkalies at the test temperature, it is possible to determine whether the solution is saturated or oversaturated with calcium hydroxide (as in the case of portland cement alone) or not saturated. In the diagram in figure 2, therefore, the points representing the composition of the contact solutions for hardened cements containing no free, easily removable calcium hydroxide must be located below the solubility isotherm.

The test proposed by N. Fratini is designed to determine whether the material with pozzolanic activity added to the portland cement, whatever its nature may be and whatever may be the mixture ratio, will actually fix the calcium hydroxide freed by hydrolysis of the portland cement. In practice the test is carried out at a temperature of 40 °C. The cement (20 g) and distilled water (100 ml) mixture, placed in glass bottles, waxed and sealed, is kept at the above temperature for varying periods in a thermostat. At predetermined times the contact solution is removed to determine the total alkalinity and the calcium hydroxide content (gravimetrically). The type of pozzolanic material mixed with the portland cement, and the mixture ratio, are satisfactory if the point representing the analyzed solution comes below the solubility curve shown in figure 2.

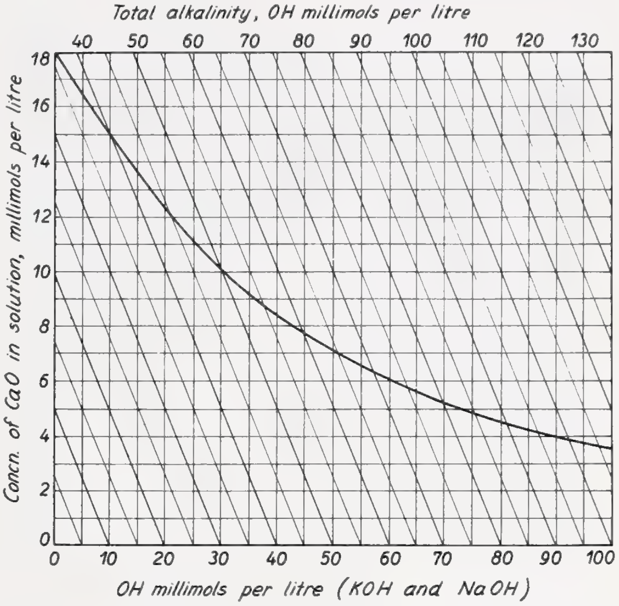

FIGURE 2. *Solubility isotherm (40 °C) for* $Ca(OH)_2$, *in the presence of alkalies.*

Pozzolanic Cements and Corrosion Resistance

It has been shown that from the qualitative aspect, the final compounds found in hardened pozzolanic cement are of the same type as those produced by hydration of portland clinker constituents.

Free calcium hydroxide is, however, contained in hardened pozzolanic cement in much reduced measure, and is protected and isolated by the newly formed pseudogelatinous products surrounding the crystallites, which prevent their passing into solution and hindering ionic diffusion.

For this reason the tobermoritic phase of hardened pozzolanic cements must have a lower lime content than that obtainable by hydration of portland cement.

Moreover, even if the end products of hardening are qualitatively the same, there must be a considerable difference in the development of the process and in the final arrangement, because while the cementitious compounds originate in portland cement exclusively from hydration of the clinker constituents, with pozzolanic cement they originate partly from the reaction between lime from hydrolysis and the active constituents of the pozzolanic material that is mixed with the portland cement.

In reacting with the free calcium hydroxide and supplementing it with low-basic, more stable compounds, the pozzolana does away with an important cause of vulnerability in hardened cement.

The newly formed, pseudogelatinous, expanded products tend to fill up the spaces between the original grains of portland cement and pozzolana, and to fill the micropores of the mortar and concrete, thus aiding in reducing permeability, and enhancing corrosion resistance.

This particular texture, in conjunction with elimination of potentially attackable calcium hydroxide, may account for the improved resistance attained by mixing pozzolanic materials with portland cement.

That the nature of the products of the reaction between pozzolanic constituents and the lime liberated during clinker hydration does produce a difference in the texture of the two types of hardened cement, i.e., pure portland and pozzolanic cement, is confirmed by the results of a systematic series of percolation tests made by F. Arredi [65] with concrete made up in the same way, the only difference being in the type of cement; and by L. Santarelli and C. Cesareni [66] with mortars prepared from different cements, including pozzolanic types.

The protective action of the tobermoritic, low-crystallized phase, with respect to more vulnerable constituents in hardened pozzolanic cement has been confirmed by observations made by

B. Tavasci and A. Rio [67, 68], who emphasize the greater resistance of pozzolanic cement (which is less basic than portland and above all contains far less free calcium hydroxide) in withstanding decalcification due to leaching conditions.

It has already been repeatedly stated that pozzolanic cements do not possess any intrinsic, specific, chemical resistance to attack by sulfates. The reactive alumina of pozzolana is, in fact, found in hardened cement, in the form of potentially vulnerable calcium aluminate.

Nevertheless, as calcium hydroxide gradually disappears with the development of the pozzolanic action, the conditions set up may be unfavorable to the formation and stability of expansive sulfoaluminate.

The cement's reduced basicity and low content of free calcium hydroxide, as well as the protective and waterproofing action of the newly formed compounds—a protection which undoubtedly hinders and slows down ionic diffusion, i.e., exchange with the contact solution—are likewise factors in support of probable higher resistance to sulfate attack, which can be achieved by mixing pozzolana with portland cement [69].

It may likewise be expected that the improvement of corrosion resistance will be enhanced according to the length of wet curing given the pozzolanic cement, because the pseudogelatinous compounds, which are not stable forms, evolve as time passes, gradually acquiring their final arrangement and probably becoming an increasingly efficient barrier to ionic diffusion.

In the light of the foregoing considerations, to improve the resistance of pozzolanic cements to sulfate attack the following points should be borne in mind:

(a) the advisability of using a pozzolanic material having very little, or no, reactive alumina;

(b) the advisability of using a clinker with a low C_3A content in portland-pozzolana mixture.

To determine the mixture ratio, useful data can be obtained with the test suggested by N. Fratini.

Pozzolanas as Additives to Prevent Expansion Caused by the Alkali-Aggregate Reaction

Additions of pozzolanic material to portland cement are today advised as a suitable means for preventing expansion, and the cracking caused thereby, that result from reaction of the reactive silica contained in certain aggregates with the alkalies present in the cement.

When pozzolanic materials having little or no alkali are added to the cement, such as, for instance, diatomaceous earths, certain burnt clays, certain types of fly ash, etc., the pozzolana will have the effect of inhibiting reaction between the alkali of the cement and the reactive aggregate by retaining at least a good part of the alkalies, so as to diminish the quantity thereof in the contact solution, and hence the extent and rate of attack on the surface of such aggregates as may be susceptible to alkali attack. More precisely, the alkalies will be partly dissolved in the contact solution and partly retained by the products of the reaction of the calcium hydroxide with the pozzolana, more particularly by the calcium silicate hydrate, forming weakly soluble compounds.

Natural pozzolanas and volcanic tuffs contain considerable percentages of alkali which are released by the transformation occurring in the material during the hardening process of pozzolanic cement, and it has already been seen that the quantities thus freed are conspicuous. If the pozzolanic cement has been prepared with materials like the Italian pozzolanas and "trass", for instance, which in reacting with calcium hydroxide give up a large part of their alkalies, the protection afforded by the reactive aggregates suggested in the foregoing interpretation appears doubtful, the more so in that the conspicuous quantity of alkalies in the pozzolana has to be added to those in the portland cement.

However, the fact remains that in Italy, where pozzolanic materials have been used for more than two thousand years, in mortar and concrete, and have been mixed with portland cement for the past fifty years, no trouble has yet developed which could be ascribed to the reactivity of aggregates with alkalies, not even when the pozzolanic cement was mixed with aggregates like lavas, for instance, presumably containing alkali-reactive glass.

This is a field still open to further investigation.

Heat of Hydration of Pozzolanic Cements

The estimation of heats of hydration of pozzolanic cement by determining the heat of solution of anhydrous cement and of hydrated cement is not as accurate as with portland cements, because pozzolanic material is not completely soluble [70, 71, 72, 73]. Nevertheless, since both anhydrous and hydrated pozzolanic cement have about the same rate of solution, an approximate estimate of the heat of hydration can be made even without waiting until the sample has entirely dissolved. It can be assumed that the fraction of pozzolana that offers resistance to dissolution in the acid solvent, will likewise resist reaction with calcium hydroxide while the cement is hardening, and will therefore have been altered very little or not at all in the hardened cement.

A proposal was recently made [74] to evaluate the heat of hydration of pozzolanic cements by performing the hydration under conditions of no heat loss (adiabatic calorimeter). The adiabatic calorimeter used is based on the principle of keeping the sample being hydrated (a block of concrete) in surroundings automatically maintained at the same temperature as that of the sample.

The heat of hydration of pozzolanic cement depends principally on the ratio of clinker and pozzolana in the mixture and on the type of clinker.

Low heat of hydration clinkers, brownmilleritic clinkers for instance, are mixed with pozzolana to produce a cement that is used on a wide scale in Italy, especially in building dams.

Activation of Pozzolanic Materials

Proposals have been made from many sources for increasing the activity of pozzolanic materials by appropriate treatment—generally heat processes. With natural, typical pozzolanas, unless they are altered materials particularly rich in clay matter, heat treatment is ineffective; actually at temperatures about 650–700 °C the effect is definitely deleterious to pozzolanic properties.

Experiments made by Q. Sestini and L. Santarelli [75] and by R. C. Mielenz, L. P. Witte, and O. J. Glantz [28] confirm that heat treatment is useful only in the presence of clay materials which acquire pozzolanic properties pursuant to dehydration.

R. Turriziani and G. Schippa [76] have studied the thermal behavior of Roman pozzolanas (leucititic) treated up to 750 °C for varying periods. They investigated the density, calcium-fixing ability, and setting times of mortars made up with treated pozzolanas, finding that while treatment up to about 400 °C did not change the activity of Roman pozzolanas, higher temperatures had a detrimental effect in that they notably diminished the rate at which calcium hydroxide was fixed and the reactivity to acid-basic attack, while the density appeared to be augmented. These effects are all the more marked the higher the temperature and the longer the time of heat treatment.

K. M. Alexander [77] has proposed strong acid treatment to activate materials having weak pozzolanic activity or none at all. The acid attack on decomposable silicates releases gelatinous silica, which is responsible for the pozzolanic activity of the material thus treated. However, for practical and economic reasons, this treatment does not seem to have much prospect of success beyond the laboratory.

Pozzolanic Cements in Practical Applications

Low heat of hydration and enhanced resistance to corrosion relative to ordinary portland cements are the two characteristics which distinguish pozzolanic cement and account for its wide-scale use in the bigger types of concrete constructions like dams and marine works.

The particular texture of the hardened cement, viz, the presence of pseudo-gelatinous formations which tend to fill the empty spaces, gives better waterproofing action than standard-mixture concretes, a quality that is especially valuable in works which have to withstand continual contact with water. In Italy, impressive amounts of pozzolanic cement have been employed over the past fifty years precisely for the above uses, and results have always been entirely satisfactory.

However, as compared with portland cement, the portland-pozzolana mixture also has its drawbacks. Slightly more water is needed in the mixtures; drying shrinkage is greater, likewise the expansion of submerged mortars and concretes. From the standpoint of mechanical strength, not only in tamped mortar but equally in plastic mortar and concrete, pozzolanic cement is slower to harden than pure portland. Strength after short curing—more particularly in the case of plastic mortars and concrete than with tamped mortar—is decidedly less than that of the same portland cement used alone.

As hardening proceeds for further periods of time, and if the hardening is aided by storing the mortar or concrete in water, the discrepancy diminishes, then disappears, and subsequently the strength of the pozzolanic material is greater than that of mortars and concretes made with pure portland cement, all other conditions being equal. Increases in tensile strength are generally greater than those in compressive strength.

If, on the other hand, the mortar or concrete remains in the open air, the pozzolanic cement will have lower strength than pure portland, even after long curing. When used in construction exposed to the air, the pozzolanic addition should not be considered completely inert and therefore purely a diluent of the cement, because the concrete, and in particular the cement in it, retains some free water which is the vehicle by which the lime hydrolysis of the clinker is able to attack the pozzolana grain.

The newly formed, pseudogelatinous products which envelop the grain and, expanding, fill the empty spaces, are in turn both the cause and the site of the phenomena of adherence about which we know nothing, so we are unable to assess their undoubtedly considerable influence on the strength of the hardened cement. For example, it is well known that by using clinker as an aggregate extremely strong concretes are obtained [78, 79].

It may further be recalled that with pozzolanic additions such as diatomaceous earths, the workability of the pastes can be improved and the tendency of the aggregates to segregate reduced, at the same water-cement ratio [80].

With regard to frost resistance, concretes made from pozzolanic cements and air cured are considered more sensitive than those made of pure portland cement, although this undesirable characteristic can be repressed by the use of air-entraining agents.

The physico-mechanical properties of portland-pozzolana mixtures obviously depend on both the type of clinker and the type of pozzolanic material, as well as on the mixture ratio.

Undoubtedly the lack of reliable criteria for predicting the behavior of pozzolana when mixed with portland clinker has in the past limited and still inhibits wider use of pozzolanic cements beyond specific applications like marine works and the larger types of cast concrete constructions.

It must be admitted that with our present knowledge it is still impossible to estimate accurately the most suitable mixture ratio for a given clinker and a particular type of pozzolana in order to obtain optimum cementitious properties.

This ratio has to vary not only with the type of the two materials mixed, clinker and pozzolana, but also in accordance with the end purpose of the cement, which may call for enhancement of one, or a limited number, of quality characteristics.

Actually, the technology of the production of cement has forged ahead of its application so that only in special cases like thin, light prestressed structures, which so far do not constitute the greater part of the total, is quick-hardening cement with high initial strength called for. In the majority of end uses, the advantages accruing from very high strength would be questionable if they were to give rise in practice to an unduly low cement content in the concrete, or inappropriate reduction in the size of the structures, with the same concrete mixture ratios [81].

In endeavoring to augment concrete strength by means of the cement factor only, it should be considered that as a rule the initial strength of portland cements with high hydraulic value is accompanied by negative characteristics, such as high heat of hydration with its ensuing thermal effects, increased drying shrinkage, and diminished corrosion and frost resistance, all factors which are closely related to the life of the construction.

In Italy, pozzolanic cements, which are classified under proper standard specifications demanding a composition ratio (portland-pozzolana mixture) with a high pozzolana content, have for many years been widely employed not only for the specific end-uses referred to in the foregoing, but also for all kinds of air-cured constructions.

In other words, this cement stands on the same footing as portland in satisfying the demands of a considerable part of the cement uses contemplated by current building techniques.

However, developments in these techniques, and the ensuing demand for higher strengths, may, and probably will at some future time, lead to a further quality differentiation between pure portlands and pozzolanic cements.

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Discussion

W. C. Hansen

The statement by the author that pozzolans produce "pseudogelatinous formations which tend to fill the empty spaces" suggested the idea of calculating the porosities of hardened cement pastes made without and with pozzolans. In these calculations, it was assumed that SiO_2 forms $C_3S_2H_3$ and that Al_2O_3 forms either C_3AH_6 or C_4AH_{13}. It was also assumed that SiO_2 and Al_2O_3 in glasses, altered tuffs, and activated clays have somewhat lower densities than those of quartz and corundum. The values used for the densities of the various compounds are as follows:

Compound	*Density*	*Compound*	*Density*
$Ca(OH)_2$	2. 23	C_4AH_{13}	2. 08
C_3S	3. 15	S	2. 31
$C_3S_2H_3$	2. 44	A	3. 50
C_3AH_6	2. 52		

The first four were taken from Lea [1],[1] the fifth from Roberts [2] and the others from a chemical handbook [3].

The calculations were made on the basis that the cement was pure C_3S, that clays have the composition AS_2, that the water content of the cement paste was 40 percent by weight of solids (cement plus pozzolan), and that the decrease in the volumes of the reactants upon combination exists as void spaces in the hardened paste. In other words, it is assumed that the volume of the undried hardened paste equals the sum of the volumes of the reactants (solids plus water) and consists of solid reaction products, uncombined water, and void space with the sum of the last two representing the porosity.

Calculations were made for six reactions as follows:

$$\begin{array}{ll} & 2(C_3S)+6H=C_3S_2H_3+3CH \\ \text{Weights} & 456\ +108=342\ +222 \\ \text{Volumes} & 144.7\ +108\quad 140.2\ +99.5 \\ \multicolumn{2}{l}{\text{Void Space}=(144.7+108)-(140.2+99.5)=13.0} \end{array} \tag{1}$$

$$\begin{array}{ll} & 2(C_3S)+2S\ +6H=2(C_3S_2H_3) \\ \text{Weights} & 456\ +120+108=\ 684 \\ \text{Volumes} & 144.7\ +\ 52+108\quad 280.4 \\ \multicolumn{2}{l}{\text{Void Space}=(144.7+52+108)-280.4=24.3} \end{array} \tag{2}$$

$$\begin{array}{ll} & 2(C_3S)+\ A\ +9H=C_3S_2H_3+C_3AH_6 \\ \text{Weights} & 456\ +102\ +162=\ 342\ +\ 378 \\ \text{Volumes} & 144.7\ +29.1+162\quad 140.2\ +\ 150 \\ \multicolumn{2}{l}{\text{Void Space}=(144.7+29.1+162)-(140.2+150)=45.6} \end{array} \tag{3}$$

$$\begin{array}{ll} & 8(C_3S)+\ 3A\ +51H=3(C_4AH_{13})+4(C_3S_2H_3) \\ \text{Weights} & 1824\ +306\ +918=\ 1680\ +\ 1368 \\ \text{Volumes} & 478.8\ +87.4+918\quad 807.7\ +\ 560.8 \\ \multicolumn{2}{l}{\text{Void Space}=(478.8+87.4+918)-(807.7+560.8)=115.7} \end{array} \tag{4}$$

$$\begin{array}{ll} & 14(C_3S)+\ 3(AS_2)\ +69H=3(C_4AH_{13})+10(C_3S_2H_3) \\ \text{Weights} & 3192\ +\ 306+360\ +1242=\ 1680\ +3420 \\ \text{Volumes} & 1013.3\ +87.4+155.8+1242\quad 807.7\ +1401.6 \\ \multicolumn{2}{l}{\text{Void Space}=(1013.3+84.7+155.8+1242)-(807.7+1401.6)=289.2} \end{array} \tag{5}$$

$$\begin{array}{ll} & 4(C_3S)+AS_2\ +15H=3(C_3S_2H_3)+C_3AH_6 \\ \text{Weights} & 912\ +222\ +270=\ 1026\ +\ 378 \\ \text{Volumes} & 289.4\ +81.0+270\quad 420.6\ +\ 150 \\ \multicolumn{2}{l}{\text{Void Space}=(289.4+81.0+270)-(420.6+150)=69.8} \end{array} \tag{6}$$

Table 1.

Reaction No.	Weight of solids	Volume of water [a]	Volume of reactants	Volume of combined water	Volume of free water	Volume of voids	Volume of total pores	Percent [b] porosity by volume
1	456	182. 4	252. 7	108	74. 4	13. 0	87. 4	34. 5
2	576	230. 4	304. 7	108	122. 4	24. 3	146. 7	48. 1
3	558	223. 2	335. 8	162	61. 6	45. 6	107. 2	31. 9
4	2, 130	852. 0	1, 484. 2	918	−66. 0	115. 7	(c)	(c)
5	3, 858	1, 543. 2	2, 498. 5	1, 242	301. 2	289. 2	590. 4	25. 2
6	1, 134	453. 6	640. 4	270	183. 6	69. 8	253. 4	39. 5

[a] 40 percent by weight of solid reactants.

[b] Volume of voids plus volume of free water as percent of volume of reactants (solids plus water).

[c] 40 percent water is insufficient for complete reaction.

The data from the calculations give rise to table 1.

From these calculations, one might draw the following conclusions regarding the influence of pozzolans in producing hardened pastes with porosities below those of hardened pastes of portland cements:

(1) A highly siliceous pozzolan is harmful.

(2) A highly aluminous pozzolan is beneficial if the reaction product of the alumina is C_4AH_{13} and only slightly beneficial if the product is C_3AH_6.

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[1] Figures in brackets indicate the literature references at the end of this paper.

(3) An aluminous product with an A/S ratio of 1:2 is beneficial if the reaction product of the alumina is C_4AH_{13} but harmful if the product is C_3AH_6.

The author points out that, compared to portland cements, the portland-pozzolan cements require more water, have greater drying shrinkage and greater expansion when submerged in water. Some investigators have visualized this expansion as filling void space. Lea [4], following a theory by Lafuma, pictured the solid grain of pozzolan reacting in the hardened paste with dissolved $Ca(OH)_2$ to form solid products *in situ* which, upon crystallizing, exert a thrust against the surrounding solids. This mechanism of the reaction appears to be correct, but it is difficult to see how this expansion would have much, if any, effect in decreasing the space classed as voids and the space occupied by uncombined water in the hardened paste.

It seems that the results for porosities obtained from these calculations should indicate approximately what is to be expected from pozzolans of different compositions. If this is true, then the influence of a given material on such properties as strength, resistance to leaching by water, resistance to attack by sulfates, and resistance to freezing and thawing might be predicted in a general way from information regarding the amounts of reactive SiO_2 and Al_2O_3 in the product. Any material that tended to increase the porosity of the hardened paste would be expected to be harmful with respect to those properties. These calculations have not taken into account the effects of any inert materials that might be present in commercial pozzolans.

The author points out that the alkali content of the pozzolan may play a substantial role in the kinetics of the reaction with $Ca(OH)_2$. It seems that this might be particularly true for glasses and that the alkali content of the cement may also have a marked effect upon the rates at which glasses are converted to calcium compounds. Alkalies in the cement that are released to the water will increase the OH^- ion concentration in the liquid phase and make it more aggressive toward the glass. They will also decrease the Ca^{2+} ion concentration, which would tend to retard the rate of conversion to calcium compounds. However, the increase in OH^- ion concentration probably has a greater effect than the decrease in the Ca^{2+} ion concentration.

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Discussion

N. R. Srinivasan

I will confine my remarks mainly to the following three points:

(1) Certain aspects of the structure of pozzolanic materials.

(2) The relationship between pozzolanic action and cement hydration.

(3) The resistance to sulfate attack as offered by the pozzolanas.

In the course of a past investigation [1, 2][1] at the Central Road Research Institute, New Delhi, on the pozzolanic properties of burnt clay powder (Surkhi), many of the earlier findings of Mielenz and others [3] regarding the relationship between the structural collapse of the clay and its pozzolanic activity were confirmed. In addition, it was pointed out that the structural defects, including the strain in the bonds that accompany the dehydration of clays, greatly influence pozzolanic activity. Thus it was suggested that the conditions governing pozzolanic reactions are the same as those that govern the solid-state reactions.

Experiments on different samples of the individual oxides, viz, silica, alumina, and iron oxides showed, as expected, widely differing reactivity for the different samples of the same oxide. This variation was attributed to the different structural and surface conditions which are greatly interrelated. Among these oxides, silica from silicic acid gels showed by far the greatest reactivity. Alumina and iron oxides of certain forms exhibited a limited degree of reactivity. Some natural aluminosilicates like kaolin showed, after burning at optimum temperature, the highest reactivity. This is in line with the evidence presented in this paper wherein the presence of "reactive alumina" (which could reasonably be taken as the low-temperature form of gamma alumina and related forms) is said to enhance the reactivity of the pozzolana. The reactivity in all these cases was measured by determining the compressive strengths of lime-pozzolana mixtures.

At present some work is being done to study certain parallels that seem to exist between the required structural conditions for an effective silica-alumina cracking catalyst and an effective pozzolana. It is true that catalytic and pozzolanic reactions are entirely different from each other. The catalyst is a foreign body which without any apparent change presents a surface with 'active spots' where reactions between the components can take place more rapidly. The pozzolan on the other hand is part of the reacting system that undergoes permanent changes through new chemical bonding with hydrated lime. But part of their mechanisms may have something in common as is indicated by the following.

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[1] Figures in brackets refer to the literature references at the end of this paper.

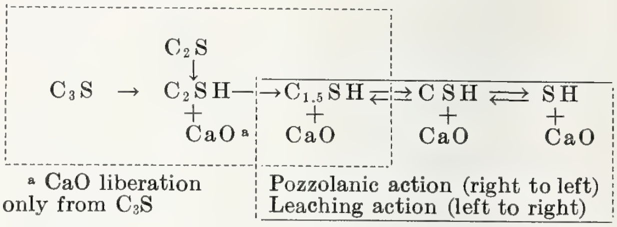
It is known that neither silica nor alumina by itself is as good a catalyst as a proper combination of both. The silica-alumina catalysts obtained through coprecipitation have in them the $\geqslant$Si—O—Al$\leqslant$ bonds, which could not be formed if both or either of the oxides were anhydrous to begin with. In the case of clay catalysts, their modes of preparation are strikingly similar to those of clay pozzolans, both of which need acid treatment and/or dehydration. In all the preparations, the Al ion is said to occupy a tetrahedral position, which is held to be an essential condition for catalytic reaction [4]. This structural defect has been shown to involve the movement of the O ions by a few tenths of an angstrom and consequent strain in the bonds [5]. The AlO_4 part also needs a H ion to balance the electrical charge, and this ion imparts the 'acid' character to the catalyst [4]. This H ion plays an important part in the reactions. Many of the said factors may also facilitate chemical bonding of the molecules with the surfaces, and thus affect both pozzolanic and catalytic reactivity. It appears that the mode of bonding will be explained in due course by the principles of the solid state and semi-conductors.

If it is accepted that the reactivity is mainly controlled by structural defects, it is possible to explain some anomalies regarding pozzolans and cements. It explains, for instance, the apparent difference between the different types of pozzolans. The reactivity of the natural pozzolans of volcanic origin could mainly be attributed to the high degree of structural disorder that is known to exist in the glassy phase. Thermal treatment of these products may often result in the release of the excess strain in bonds and a somewhat more orderly structural arrangement as happens during the process of annealing, and may thus adversely affect reactivity. The present paper shows that such reduction in reactivity does take place. Pozzolanas like opal, chalcedony, diatomaceous earth, etc., are mainly composed of hydrated silica and may thus behave similar to silica gels. Dehydration of these brings about special surface conditions with defective structure conducive to enhanced reactivity. Those like clays, bauxite, etc., also need dehydration accompanied by complete or partial collapse of the structure, so that highly reactive forms of silica, alumina, or a complex remnant structure of the alumino-ferrosilicate, all characterized by a highly defective structure, could be left behind.

In the case of cement compounds, the varied structural investigations have more or less established that structural defects, such as the irregular coordination of ions which leave structural "holes" and bond strains, and the tetrahedral coordination of Al in certain structures, are effective in promoting hydration reactivity. Similar defects seem to affect pozzolanic reactivity as well.

The final products of both cement hydration and pozzolanic reaction appear to be the same, as has been pointed out in this paper, even though the course of their formation is different. A combined picture of the two reactions could be given as below:

Cement Hydration (left to right)



ᵃ CaO liberation only from C_3S

Pozzolanic action (right to left)
Leaching action (left to right)

Sulfate resistance. Till now it was held that use of burnt clay in concrete was one of the measures to counteract sulfate attack. An extensive investigation at the Central Road Research Institute [6] has shown that clays calcined at 600–800 °C were not as effective in preventing sulfate attack as those burnt at 1,000 °C. In fact, with certain clays like kaolins burnt at 600–800 °C, the concrete suffered greater damage than in the case of plain concrete. The following explanation appears to be close enough to the one indicated in this paper.

At 1,000 °C, the alumina released from any clay after structural disintegration is in the high-temperature gamma form or alpha form, both with a comparatively better crystallinity, ordered structure and reduced reactivity. Thus the alumina in clays calcined at 1,000 °C is not able to combine effectively with the CaO and SO_3 to form the expansive sulfoaluminate. At lower temperatures, the alumina is in the highly reactive, microcrystalline, low-temperature form of gamma alumina with defective spinel structure. In the system $CaO–Al_2O_3–CaSO_4–H_2O$, it is reasonable to expect marked reaction, leading to ettringite formation, only with the reactive form of gamma alumina as obtained from clays calcined at a lower temperature.

With the above explanation it appears as if the dehydrated clay structure, despite its complex nature, is so highly strained that the bonds get broken and the individual oxides get separated easily, thus giving the components for the $CaO–Al_2O_3–CaSO_4–H_2O$ system.

Other reasons may include the type of sulfoaluminate formed (ettringite or the low-sulfate type) depending upon the concentration of the lime solution in the vicinity of the reaction.

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Discussion

L. Santarelli

Prof. Malquori's paper refers to the methods used to measure the heat of hydration of pozzolan cements and dwells on the difficulty accompanying the solution method, due to the incomplete solubility of these cements.

Malquori points out a weak point in the determination of the heat of hydration of pozzolan cements and it seems, therefore, opportune to return to the subject, due to the undeniable importance that the measurement of the heat of hydration has on the use of pozzolan cements in the construction of dams.

Two studies [1,2] [1] on the subject appeared after Malquori's paper had been presented to this Symposium, and I wish to refer to them in this discussion. They propose a modification of the ASTM method and present a new thermometric method known as the "Controlled dispersion thermometric method."

The main modification of the ASTM method consists in maintaining constant the temperature of the surroundings of the reaction vessel, extending the solution period to two hours so as to reduce to a minimum the insoluble residue due to the pozzolan (this extension is rendered possible by the thermostatic bath which facilitates the correction system), and adopting a special device for the introduction of the sample in the acid mix.

The adoption of these modifications permitted the substantial reduction of the strong variations which occur in the measurement of the heat of hydration by the solution method.

The table 1 shows the dispersion coefficients observed with two pozzolan cements (prepared with the same clinker and two different pozzolans), compared with those of portland cement (prepared with the same clinker used in the pozzolan cements).

It is worth remarking that in the previous tests with the solution method (not modified) by the same operator, the average dispersion for pozzolan cements was 10 times as high.

The second study concerns the elaboration of a method which would not require particular chemical operations as does the solution method and which also would permit the following of the evolution of heat during the initial stage.

With the apparatus shown in figure 1, it is possible to follow the thermal process of hydration from 15 minutes to 28 days.

Adopting spherical Dewar vessels, it was possible to obtain very low dispersion coefficient values K (8–10 cal/deg/hr) permitting the making of measurements up to 28 days.

Table 1. *Standard deviation (σ) and coefficient of variation (σ%) values (modified solution method)*

Sample	Heat of solution (average figures for anhydrous cement and hydrated cement at 7 and 28 days)		Heat of hydration (average figures at 7 and 28 days)	
	σ	σ%	σ	σ%
Pozzolan Cement L	1.37	0.26	1.57	2.73
Pozzolan Cement F	1.03	0.19	2.11	3.52
Portland Cement	0.79	0.14	1.12	1.44

The thermal capacity of the Dewar vessels is determined by the cold water plus hot water mix method: with this calibration method the dispersions obtained calculating thermal capacities are $<$0.2 percent.

Table 2 shows the statistical data obtained in two series of tests run with this method on one portland and one pozzolan cement.

A noticeable decrease of the σ percentage value for pozzolan cements in comparison with the solution method may be seen, while for the portland cement practically the same values are obtained (the increase of 0.33 can not be considered a significant difference).

Table 2. *Heat of hydration and σ and σ% values (thermometric method)*

Cement	Days	Calorimetric vessel					Average σ	σ %
		1	2	3	4	5		
		cal/g	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	
Portland	3	61.96	62.17	61.94	60.42	60.29	61.36±0.92	1.50
	7	70.10	69.52	69.52	69.79	67.24	67.14±1.45	2.11
	14	73.22	72.86	73.37	70.61	71.13	72.24±1.27	1.75
	21	74.61	74.10	75.14	72.01	72.96	73.76±1.27	1.72
	28	75.99	74.98	76.16	72.84	74.35	74.86±1.35	1.80
								$\overline{X}$=1.77
Pozzolan	3	36.58	36.90	36.22	37.00	36.61	36.66±0.31	0.84
	7	45.99	46.90	45.39	46.76	46.90	46.39±0.67	1.44
	14	52.66	53.50	51.75	53.53	53.95	53.08±0.88	1.65
	21	55.31	56.06	54.34	56.12	56.65	55.70±0.89	1.60
	38	56.21	57.13	55.50	57.28	57.80	56.78±0.96	1.69
								$\overline{X}$=1.44

Comparing the results obtained with this and the solution method we may see the influence of the higher temperature reached by the cementitious paste with the thermometric method (maximum temperature 30–32°) and of the initial period of 15 minutes, during which the cementitious paste remains outside the Dewar vessels (which in reality takes place also in practice). Studies to examine thoroughly the influence of these variables with the aim of rendering comparable the two methods are in progress.

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[2] L.Santarelli, Méthodes pour la mésure de la chaleur d'hydratation, Cong. Intern. Ciment, Lisbon, Aug. 29–Sept. 3, 1960.

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[1] Figures in brackets indicate the literature references at the end of this paper.

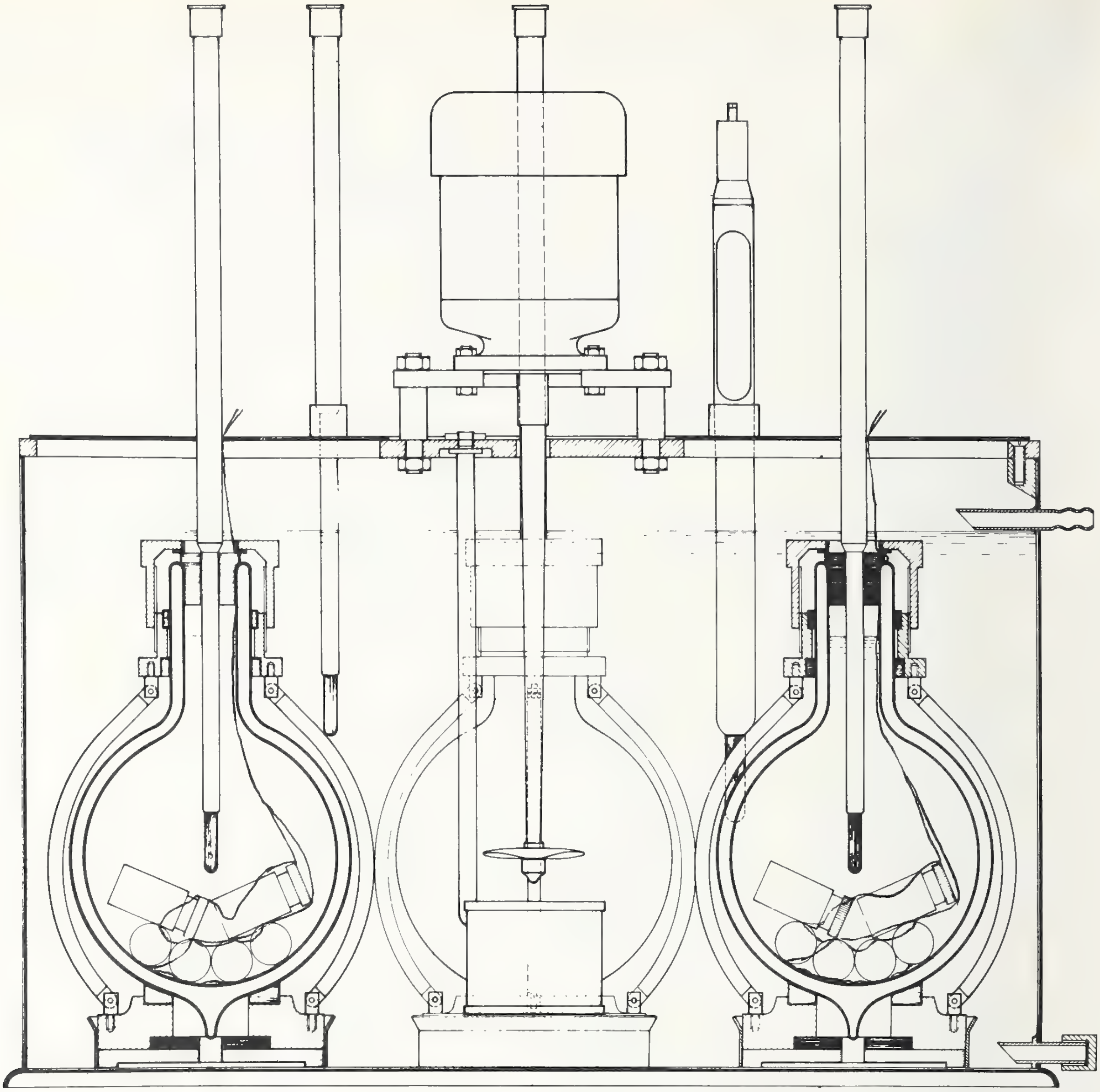

FIGURE 1. *Cross section of thermostat showing the details of the thermos bottles with containers for the cementitious paste.*

Discussion

H.-G. Smolczyk

Professor Malquori's excellent paper is of high interest to us, especially with regard to a comparison between pozzolan cements and blast-furnace slag cements. In his paper Professor Malquori states ". . . glassy (blast-furnace) slags with hydraulic properties are in themselves sufficiently basic and therefore have but a weak pozzolanic activity, in the sense of their ability to combine with lime coming from the saturated contact solution." We are also of the opinion opinion that, in general, basic blast-furnace slags show less ability to combine with lime than do highly active natural pozzolans. But well-composed, highly hydraulic blast-furnace slags do bind CaO, too, while hydrating, and this particular property can lead to the fact that mortars made of low-clinkered blast-furnace slag cements with a high percentage of well granulated slag contain but a very small amount of $Ca(OH)_2$.

The well-known capacity of good blast-furnace cements to resist various aggressive fluids can to a certain extent be explained by this property.

In figure 1 the results of some experiments are represented by graphs. A good hydraulic granulated slag, with varying admixtures of the same clinker and the same gypsum content, was ground, and the free $Ca(OH)_2$ was measured after 3, 7, and 28 days of water storage and plotted

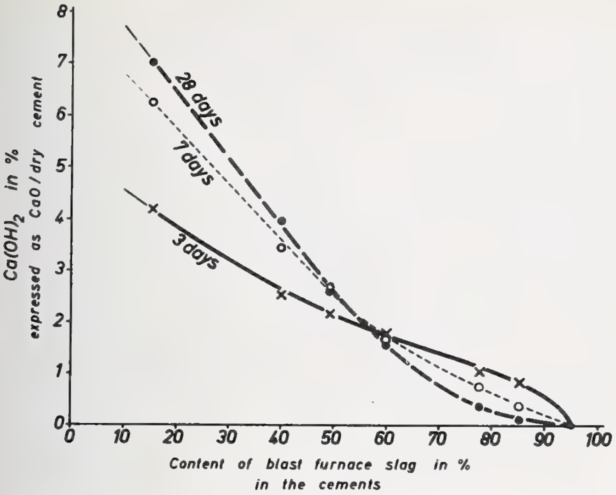

FIGURE 1. *Pozzolanic activity of a granulated-base blast-furnace slag with high activity.*

against the slag content. The graphs show the double influence of hydraulic blast-furnace slags: First, the content of newly formed soluble lime decreases in any of the three test periods in relation to the lower clinker content of the cements. If, on the other hand, reference is made to the change of the $Ca(OH)_2$ content with increase in the period of storage, the high-clinker slag cements exhibit a continuous increase of $Ca(OH)_2$, whereas low-clinker blast-furnace slag cements suffer a reduction, and, in the most extreme case, may approach zero.

Discussion

E. Burke

I should like to emphasize the importance of the author's statement that two factors must be measured in the evaluation of a pozzolanic cement; namely, the pozzolanicity which can be measured by the method described and which has been accepted by the International Standards Organization, and the mechanical strength.

In evaluating the mechanical strength attention needs to be directed to practical manufacturing conditions. In assessing the value of a pozzolana it is usual to test it by grinding or mixing it with a portland cement clinker or cement and comparing it with the same cement without pozzolana. Pozzolanas vary very greatly in their grindability so that a specific surface test is not of great value and even a sieve test is not without difficulties. The method we have used is to standardize the amount of energy used in the grinding; e.g., in a laboratory mill the total number of revolutions is the same for both the control portland cement and for the pozzolana cement.

A useful test to determine when the pozzolana contributes to the mechanical strength is to calculate or determine the strength of the control portland cement at the water/cement ratio used with the pozzolana cement, assuming that the pozzolana is part of the aggregate, i.e., the water/cement ratio is calculated on the portland cement portion only. In many of the pozzolanic materials we have tested so far we have found that no strength is contributed by the pozzolana until after 7 days but in the case of the very reactive Italian pozzolanas there is distinct contribution to strength even at three days.

The author's statement that the compounds formed on the hydration of pozzolana cements are essentially the same as those in the case of portland cement can be confirmed. One would, therefore, expect that, if the portland cement portion is a sulfate resisting type, much improved resistance would be obtained. The higher resistance of pozzolana cements made with ordinary portland cement must be attributed largely to the smaller amount of free calcium hydroxide. However, we have found that cements of this type are not as resistant as the Type V cement, especially when its C_3A content is very low. It would also be interesting to know if the more reactive pozzolanas give cements less resistant to sulfates than the less reactive pozzolanas. One might expect this in the light of Srinivasan's contribution, where it was stated that clays burned at 600–800 °C gave less resistant pozzolana cements than those burned at 1,000 °C.

Closure

Giovanni Malquori

Let me thank first of all Dr. Hansen for his remark, which is of particular interest as a proposal for further investigations. He suggests the usefulness of taking into account the variation in porosity of portland-pozzolan cement pastes and concretes, as a function of the lime attack on pozzolana, in view of the fact that the "absolute volume" of the final system, which consists of the pozzolanic reaction products, is somewhat smaller than the initial one, i.e., from the sum of the starting materials' "absolute volumes."

The interpretation of the problem is rather complicated. To make, indeed, a precise distinction among the different variables affecting it, is, in practice, not easy, taking into account that the systems we are dealing with are of the greatest complexity because of the following factors: structural disorder, presence of minor constituents, and possible solid state associations. Furthermore, distinguishing stable from transient structures is likewise difficult.

Early dilatometric investigations [1] carried out in order to evaluate the "absolute volume" variation (shrinkage) during hardening of pozzolanic materials–lime pastes (ratio: 1:1), kept in excess water, showed that the shrinkage is related to the amount of reactive Al_2O_3 in the starting pozzolanic material, as well as to the water stably bound (above 105 °C) in the hardened paste, exception being, of course, made of the water bound to free $Ca(OH)_2$.

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[1] G. Malquori and F. Sasso, Volume changes during the hardening of the system: materials showing pozzolanic activity-lime-water, Ricerca Sci. 8, (II), 440 (1937).

Dr. Hansen's remark suggests the opportunity of further investigation in the field of the physical properties of pozzolana-lime and portland-pozzolan cement pastes with regard both to the kind of pozzolana and to the mixture ratio.

I agree with Mr. Srinivasan that all transformations which determine or increase disorder and structural instability—reticular deformation, defects, and so on—increase the solid reactivity.

I also agree with Mr. Burke that the decrease, and still more the elimination, of free and mobile lime in the hardened pozzolanic cement which has been kept in water, is the main factor in the interpretation of its resistance to chemical attack by the dangerous constituents of the immersing water.

I would like to add to what has been said by Mr. Smolczyk that the problem of the behavior of granulated basic slag toward lime solution has been studied a long time at our Institute in Naples, and that our results confirm Mr. Smolczyk's indications.[2]

Finally, I thank Professor Santarelli for his remark.

I conclude by apologizing for possible omissions, and for probably not having duly emphasized the importance of some topics. This is due to the amplitude of the subject dealt with.

It should also be clear that the chief aim of this report is to emphasize that the subjects which have been briefly outlined, far from being exhausted, may well be the ground of further investigation. Personally I will consider that this aim has been satisfactorily fulfilled if the report will push further researches, the results of which I hope will be presented at the next "International Symposium."

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[2] R. Sersale and P. Giordano Orsini, Hydration and transformation of blast-furnace slags by contact with calcium hydroxide solution, Atti Accad. Sci. Fis. e Mat. [III], **1**, (1960); Ricerca Sci. **30**, 1230, (1960).

Paper VIII–4. Calcium Aluminates and High-Alumina Cements*

P. Lhopitallier

Synopsis

During the past 10 yr, new studies have been made concerning calcium aluminates. Anhydrous aluminates have not been the subject of important research: however, it seems that the reality of the compound C_6A_4fS, the formula of which had been proposed by Parker, is dubious.

Hydrated aluminates, on the contrary, have been widely studied. Researches concerned especially: The equilibrium diagrams; the reality of the compound C_3AH_n (hexagonal); the dehydration of aluminates.

Concerning the equilibrium diagram in the system $CaO–Al_2O_3–H_2O$, at various temperatures, we recall that it had been studied, during the previous years, at 21 and 90 °C only. During the period between 1950 and 1959, its construction at lower temperatures was attempted. Generally, all the results confirm, roughly, the observations made previously by Bessey and Wells. However, the picture of the equilibria, first at 1 and 5 °C, then at 21 °C, permitted a definition of the region of existence of the compound CAH_{10}, the reality of which had not previously been established.

Furthermore, it appears as established now that in normal conditions of use and at ambient temperature, the hexagonal compound that is formed is CAH_{10}, the compound C_2AH_8 being only an intermediary phase of very brief existence, except in the presence of a great excess of hydration water.

As for the C_3AH_n, it is known that its existence is debated. Schippa and Turriziani have brought new data into the discussion. According to these writers, C_3AH_{12} would be in fact the monocarboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$, whose formation cannot be avoided, the hexagonal aluminates being especially responsive to the action of CO_2 in damp atmosphere. This fact justifies the interest that would be offered by the study of the quaternary system $Al_2O_3–CaO–CO_2–H_2O$.

The same aluminates are equally sensitive to the humidity of atmospheric air. The molecules of water in the hydrates seem in effect to be bound to the molecules in a very loose manner. The loss of this crystallization water, when great enough, corresponds to a change in the crystal unit, a change which can be seen in the X-ray diffraction spectra.

The identification of the hexagonal aluminates, by the method of X-ray diffraction, is therefore somewhat tricky. It is really important that the spectrum corresponding to a definite number of molecules of water may be known with sufficient precision.

Résumé

Au cours de ces dix dernières années, de nouvelles recherches ont été entreprises sur les aluminates de calcium. Les aluminates anhydres n'ont pas été l'objet de travaux importants: cependant, il semble que l'existence du composé C_6A_4fS, dont la formule fut proposée par Parker, soit sujette à caution.

Les aluminates hydratés par contre, ont été très étudiés. Les recherches ont, en particulier, porté sur: Les diagrammes d'équilibre; l'existence du C_3AH_n; la déshydratation.

En ce qui concerne les diagrammes d'équilibre du système $CaO–Al_2O_3–H_2O$ à différentes températures, rappelons que celui-ci n'avait été étudié en effet, jusqu'alors, qu'à 21 et 90 °C. Au cours de la dernière décade, son tracé a été tenté à plus basse température. D'une façon générale, tous les résultats obtenus confirment, dans leurs grandes lignes, les observations faites antérieurement par Bessey et Wells, entre autres. Toutefois, le tracé des courbes d'equilibre, à 1 et 5 °C d'abord, à 21 °C ensuite, a permis de définir le domaine d'existence du CAH_{10}, composé dont le comportement n'avait pas auparavant été examiné.

Il semble d'ailleurs établi maintenant qu'à la température ambiante et dans les conditions habituelles d'emploi des ciments alumineux, l'aluminate hexagonal qui se forme est précisément CAH_{10}, C_2AH_8 n'ayant qu'une très brève existence, sauf si la quantité d'eau d'hydratation est importante.

Pour le C_3AH_n, on sait que son existence est controversée. L'équipe italienne de Schippa et Turriziani a apporté un élément nouveau dans le débat. D'après ces auteurs, le C_3AH_{12} serait en réalité le monocarboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$, dont la formation apparaît comme inévitable, les aluminates hexagonaux étant particulièrement sensibles à l'action du CO_2 en milieu humide, d'où l'intérêt que présenterait l'étude du système quaternaire $Al_2O_3—CaO—CO_2—H_2O$.

Ces mêmes aluminates sont également sensibles à l'influence de l'hygrométrie de l'ambiance. Les molécules d'eau des hydrates semblent, en effet, liées de façon lâche à la molécule. Le départ de cette eau de cristallisation, lorsqu'il devient important, s'accompagne d'une modification des dimensions de la maille cristalline, modification qui se répercute sur les spectres de rayons X.

Il en résulte que l'identification des aluminates hexagonaux à l'aide des spectres de diffraction X devient plus délicate. Il est donc important que les spectres correspondant aux différentes proportions de molécules d'eau soient connus avec précision.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the laboratories of Ciments Lafarge, France. (This paper was presented at the Symposium by R. Rabot.)

Zusammenfassung

In den letzten zehn Jahren sind die Kalziumaluminate wiederholt untersucht worden. Es ist nicht viel über wasserfreie Aluminate gearbeitet worden, aber man hat doch herausgefunden, daß die Verbindung C_6A_4fS, deren Formel von Parker vorgeschlagen worden ist, vielleicht garnicht existiert.

Aber die hydratisierten Aluminate sind sehr oft untersucht worden, und man hat hier vor allen Dingen die Zustandsschaubilder, die Existenzfähigkeit der Verbindung C_3AH_n (hexagonal), und die Entwässerung der Aluminate untersucht.

Das Zustandsdiagramm des Systems $CaO–Al_2O_3–H_2O$ war früher nur bei 21 und 90 °C untersucht worden, aber man hatte doch zwischen 1950 und 1959 versucht, es für niedere Temperaturen zu konstruiren. Die Ergebnisse können so zusammengefaßt werden, daß die Beobachtungen von Bessey und Wells im allgemeinen bestätigt worden sind. Aber die Gleichgewichte, die bei 1, 5° und später auch bei 21 °C erhalten wurden, haben erlaubt, das Gebiet der Existenzfähigkeit der Verbindung CAH_{10}, dessen Existenz früher zweifelhaft war, zu begrenzen.

Es ist nun auch festgestellt worden, daß unter den gewöhnlichen Gebrauchsbedingungen und den vorherrschenden Außentemperaturen, die hexagonale Verbindung CAH_{10} gebildet wird; die Verbindung C_2AH_8 ist nur eine Zwischenphase, die eine sehr beschränkte Lebensdauer hat, sei es denn, daß Hydratationswasser im großen Überschuß vorhanden ist.

In Beziehung zu C_3AH_n muß gesagt werden, daß man schon immer die Existenz dieser Verbindung angezweifelt hat. Schippa und Turriziani haben neue Messungen, die etwas zur Diskussion beitragen können, unternommen. Diese Forscher behaupten, daß das sogenannte C_3AH_{12} mit der Verbindung der Formel $C_3A{\cdot}CaCO_3{\cdot}H_n$ völlig identisch sei, da man dessen Bildung ja nie vermeiden kann, weil besonders die hexagonalen Aluminate in einer feuchten Atmosphäre sehr schnell mit CO_2 reagieren. Das deutet an, daß eine Untersuchung des quaternären Systems $Al_2O_3–CaO–CO_2–H_2O$ doch sehr wünschenswert wäre.

Diese Aluminate sind auch gegen die Feuchtigkeit der atmosphärischen Luft sehr empfindlich. Es sieht so aus, als ob die Wassermoleküle in den Hydraten an die Aluminatmoleküle nur schwach gebunden sind. Wenn das Krystallisationswasser in genügendem Maße verloren geht, verändert sich die Raumgruppe, was im Röntgendiagramm erkannt werden kann.

Das hat nun zur Folge, daß das Identifizieren der hexagonalen Aluminate durch Röntgendiagramme mit Vorsicht vorgenommen werden muß. Von grosser Wichtigkeit ist hier die Bedingung, daß das Spectrum einer bestimmten Anzahl von Wassermolekülen genau identifiziert ist.

Introduction

Since 1951, in which year Steinour [53][1] published a very complete study of our knowledge of calcium aluminates and high-alumina cements, much work has been done on the subject.

We have tried to complete the study by Steinour for the period between 1950 and 1960, and the present communication was written for this purpose. We have thus attempted to assemble and to summarize the most important available data of the latter period on the following topics:

Aluminates and anhydrous cements,

Phase relations in the system $CaO–Al_2O_3–H_2O$,

Hydration process of aluminates and high-alumina cement,

Opposing views concerning the reality of a hydrated hexagonal tricalcium aluminate,

Dehydration of some hydrated aluminates and resulting effects on their structure.

We emphasize the fact that this communication is mainly a bibliographical study. In addition, we often refer to the important general publications by Kühl [29] and Lea [32] who gave, in 1952 and 1956 respectively, most useful accounts of the question at the time.

We apologize for any omission from our list of references.

Anhydrous Calcium Aluminates and High-Alumina Cements

We would only remember here the principal points of the question as they were stated by Lea in his book in 1956. In fact, very little new data has appeared since 1952—in which year Parker [42], in London, published his general study—until 1959, except perhaps those concerning the compound C_6A_4fS:[2] however, for this last, the research is not finished and the results are not yet published.

Aluminum and calcium oxides are present in roughly equal proportions, e.g., 35–40 percent, in the composition of high-alumina cements made industrially from bauxite and limestone. Besides these principal constitutents, another important one is iron, in the form of FeO or Fe_2O_3, in the proportion of about 15 percent (expressed as Fe_2O_3). The condition of iron in high-alumina cements is determined by the nature of the atmosphere in the furnace in which the cement has been calcined. These cements also contain silica (3–7 percent) and some minor constituents as titania, magnesia, and alkalis, these in much smaller proportions than in portland cement (always under 1 percent).

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The symbol f is used herein for FeO.

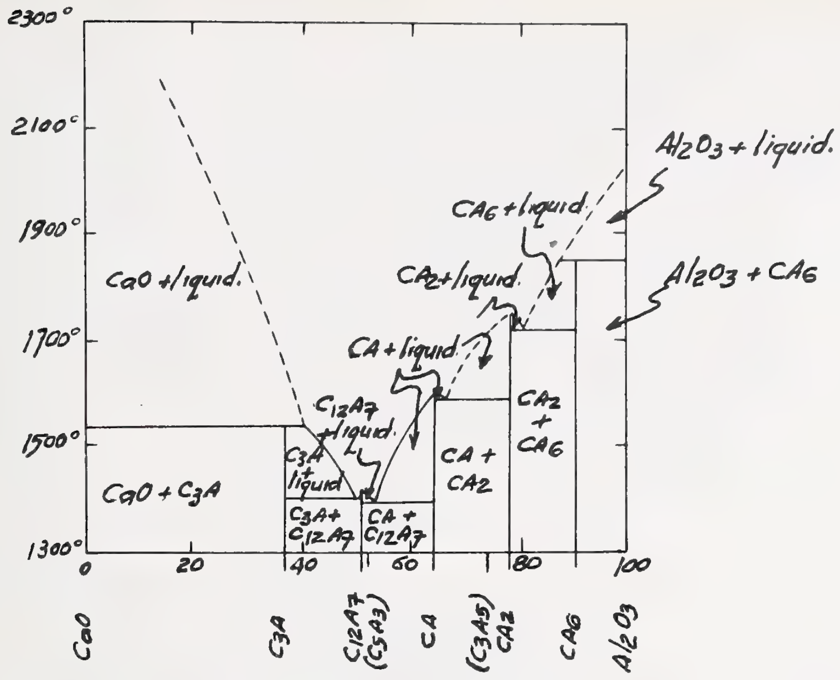

FIGURE 1. *The system* $CaO—Al_2O_3$.

After Lea [32].

Thus, the potential constituents of high-alumina cements concern not only the binary system $CaO–Al_2O_3$, but also more complex systems, of which the following have been especially studied: $CaO–Fe_2O_3$, $CaO–Al_2O_3–SiO_2$, $CaO–Al_2O_3–Fe_2O_3$, and, of course, $CaO–Al_2O_3–SiO_2–Fe_2O_3$ (these systems are illustrated in figs. 1, 2, 3, 4, 5).

Five compounds are formed in the system $CaO–Al_2O_3$, among which only four are found in high-alumina cements: $C_{12}A_7$ (formerly C_5A_3), CA, CA_2 (or C_3A_5), CA_6. The fifth, C_3A is met only in portland cements.

There is no longer any doubt about the existence of the compound $C_{12}A_7$, and the C_5A_3 formula is only retained as more convenient and because many people are accustomed to it: however, the difference between the two formulations is very little, as Lea pointed out.

"Unstable C_5A_3", resulting from the annealing of the glassy phase of clinker, was for a while confused with a pleochroic prismatic compound which may be found in high-alumina cements. Nurse and Welch show that the two compounds are, in fact, very different: "unstable C_5A_3" actually exists, but Parker, in 1952, considered the prismatic phase, already mentioned, as a solid solution which he formulated: $C_6A_4(f,M)S$. We shall consider it further.

Further, fused mixtures of composition $C_{12}A_7$ may represent a metastable equilibrium between C_3A and CA, and, under specified conditions, these two compounds may crystallize separately.

It was thought, formerly, that there exists a definite compound C_3A_5, which was then considered one of the main hydraulic constituents of high-alumina cement. It is thought now that C_3A_5 is, in fact, a mixture of CA and CA_2. Although this mixture may give high strengths, CA_2 as an isolated compound is practically inactive. The compound CA_6 has been described and studied by Filonenko and Lavrov [20].

The system $CaO–Al_2O_3–SiO_2$ gives the compound C_2AS (gehlenite) which hydrates slowly and which can be found in some high-alumina cements.

In the same way, the system $CaO–Al_2O_3–Fe_2O_3$ presents a compound C_4AF (brownmillerite) which enters the composition of high-alumina cements, as well as portland cements. It was

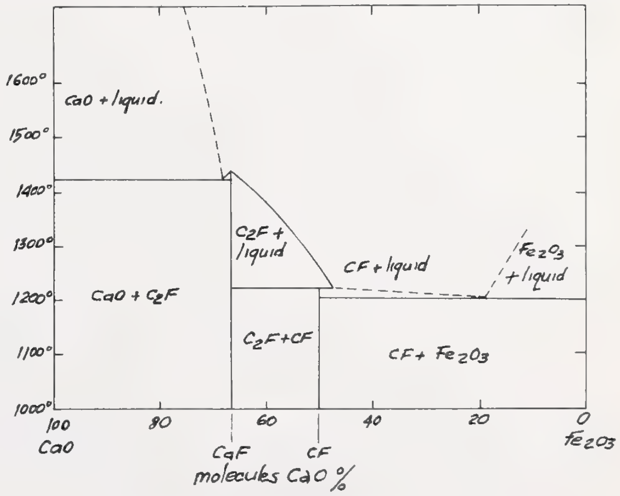

FIGURE 2. *The system* $CaO—Fe_2O_3$.

After Lea [32].

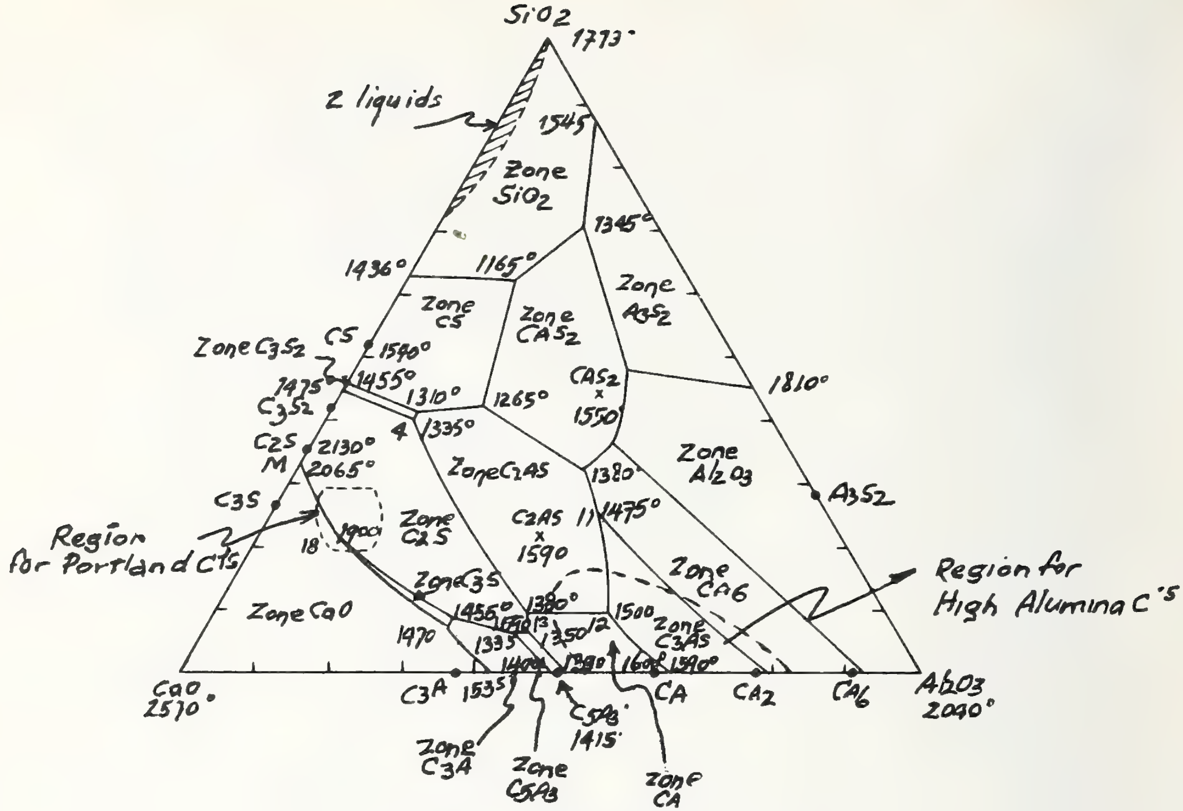

FIGURE 3. *The system* $CaO—Al_2O_3—SiO_2$.
After Lea [32].

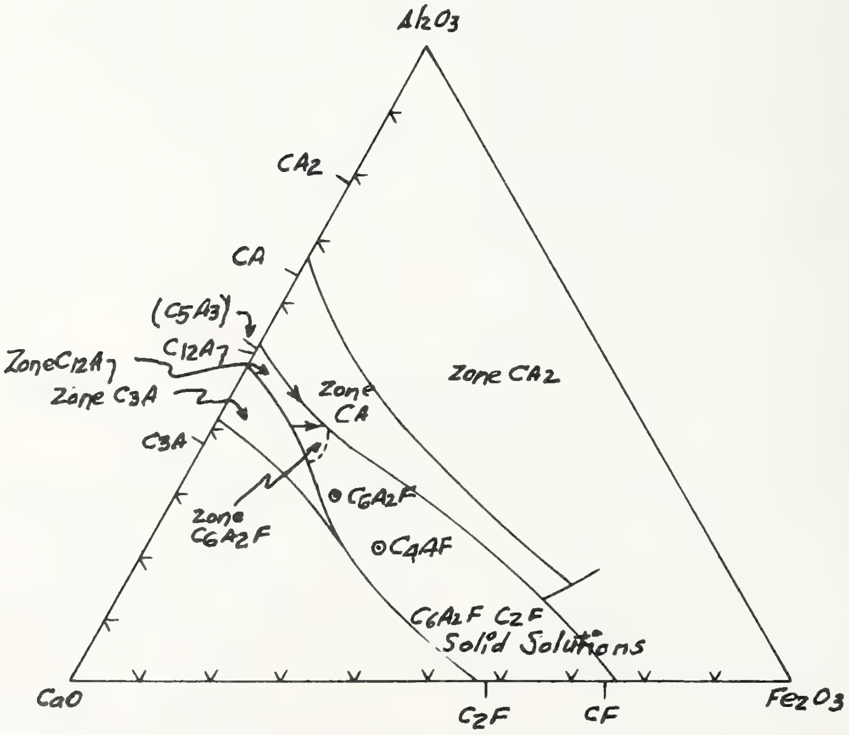

FIGURE 4. *The system* $CaO—Al_2O_3—Fe_2O_3$.
After Lea [32].

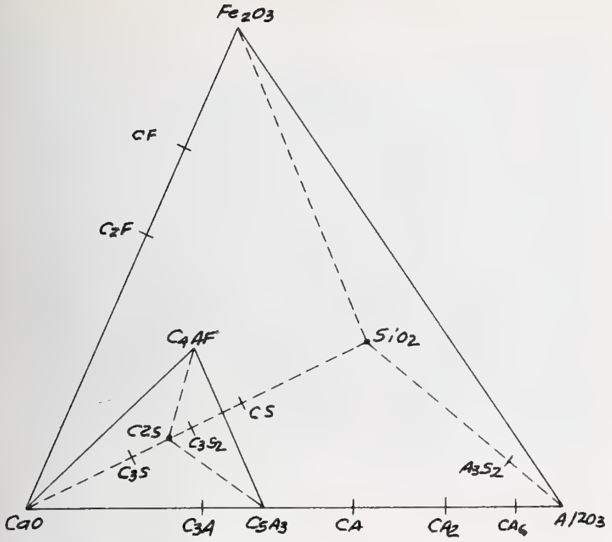

FIGURE 5. *Relation of the system* $CaO—C_2S—C_5A_3—C_4AF$ *to the greater system* $CaO—Al_2O_3—SiO_2—Fe_2O_3$.

After Lea [32].

first considered a definite compound, but it is thought now to be in fact an intermediate composition which occurs in a series of solid solutions between C_2F and a composition C_6A_2F.

The region of the system $CaO–Al_2O_3–SiO_2–Fe_2O_3$ of interest in portland cements has been extensively studied, but this is not the case for the region concerning high-alumina cement (see figs. 5 and 6). Parker, in 1952, determined the nature of the minerals present in high-alumina cement and has grouped them as follows: $CA—C_6A_4fS—C_{12}A_7—C_2S$, $CA—C_6A_4fS—C_2S—C_2AS$, $CA—C_6A_4fS—C_{12}A_7—FeO$, $C_6A_4fS—C_{12}A_7—C_2S—FeO$, $CA—C_6A_4fS—C_2AS—FeO$.

At the time, these compositions had not been accepted without reserve or divergence (see Lhopitallier and Assaud [35]).

According to Parker, the reality of a compound formulated C_6A_4fS was most probable, because of the existence of an analogous compound C_6A_4MS, TiO_2 being able to replace a part of SiO_2 in both compositions.

However, a not yet published work by Welch makes doubtful the reality of C_6A_4fS, whose formula had not been absolutely established (Robson [47]). For Welch, "unstable C_5A_3," as it has been described formerly by Rankin and Wright, is a reality as a metastable phase in the system $CaO–Al_2O_3$, and does not depend for its formation on the presence of secondary oxides. The author has not recognized the existence of solid solutions with MgO and (or) SiO_2. Solid crystals of "unstable C_5A_3" have been easily prepared on a heating-plate microscope, and optical characteristics as well as dimensions of the crystal unit have been recently published by Aruja [1].

As for the compound to which the formula $C_6A_4(f,M)S$ was given, it could not be a homogeneous compound, in spite of the fact that it contains the main part of the "fibrous constituent." Welch, however, has described a compound possibly formulated C_7A_5M, very similar to the "fibrous material" in its optical properties and, as to X-ray diagrams, presenting some similarity with C_6A_4MS. The region of stable existence for C_7A_5M would be enlarged because of the existence of a solid solution between this compound and gehlenite, C_2AS. It is thus possible to suppose that the quaternary compound is a solid solution between C_7A_5M and C_2AS.

This possibility of a solid solution is firmly supported by the following facts, according to Welch: Progressive change, observed by optical methods, of the crystalline form of the fibrous mineral along the line $C_7A_5M—C_2AS$; progressive elevation of the melting point of the mineral along this same line; progressive change of the reticular

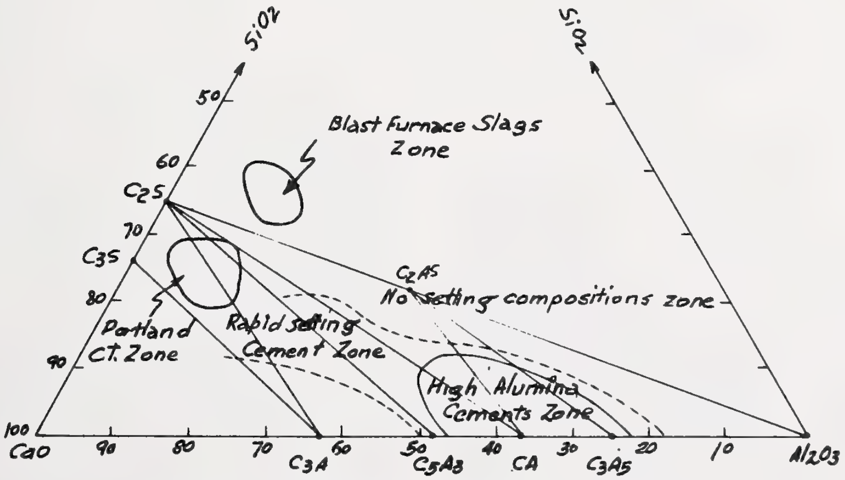

FIGURE 6. *Cement zones in the system* $CaO—Al_2O_3—SiO_2$.

After Lea [32].

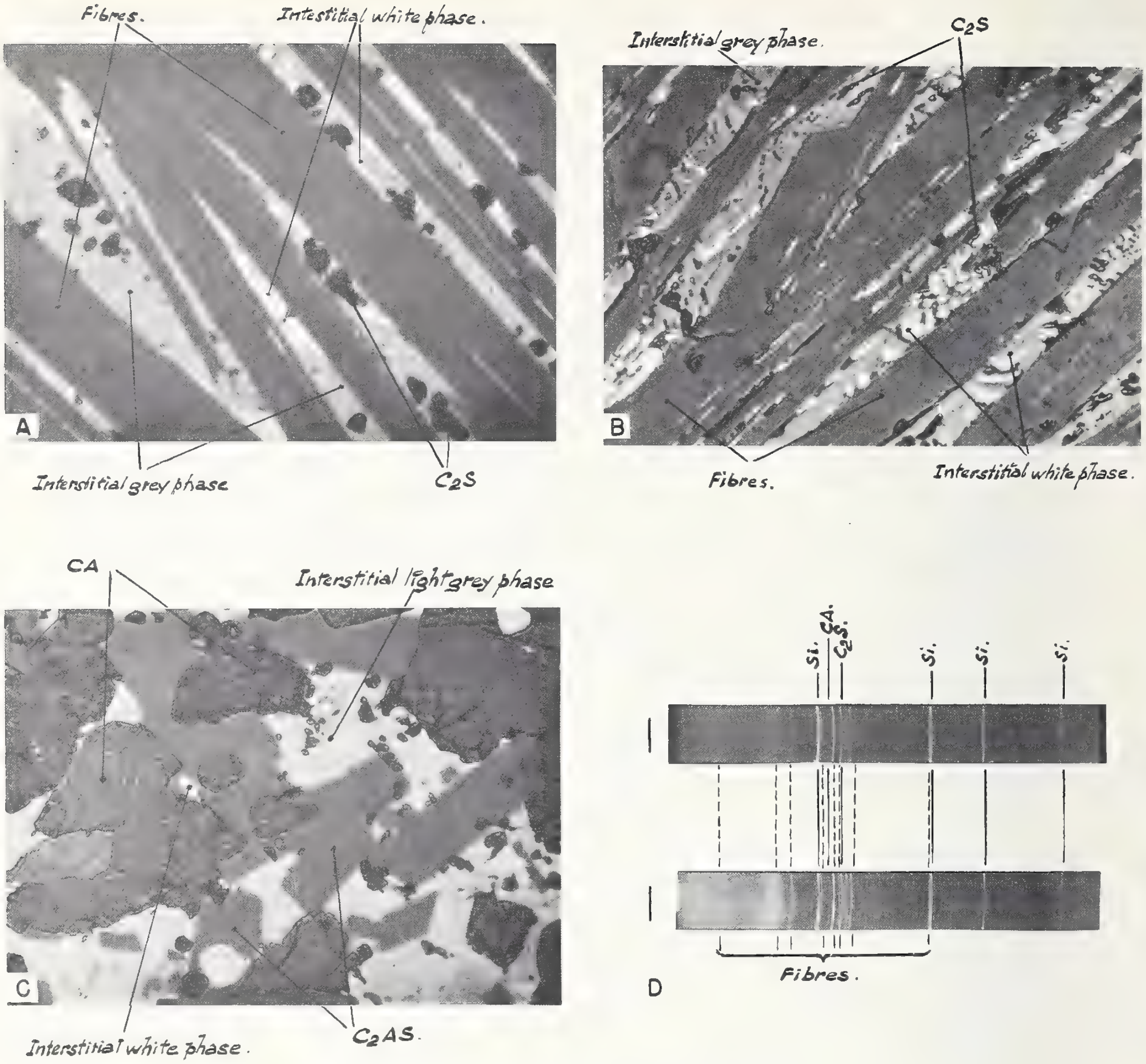
Fibres.
Interstitial white phase.
A
Interstitial grey phase
C2S
Interstitial grey phase.
C2S
B
Fibres.
Interstitial white phase.
CA
Interstitial light grey phase
C
Interstitial white phase.
C2AS.
Si.
CA.
C2S.
Si.
Si.
Si.
Fibres.
D

Plate 1. *Fused high-alumina cement after oxidizing.*

A. FeO=9.6%.
B. Annealing: 550 °C during 240 hr. FeO=0.05%.
C. Annealing: 1,300 °C during 240 hr. FeO=0.20%.
D. X-ray diagrams: Upper—fused high-alumina cement; lower—the same after annealing at 550 °C.

lengths on the X-ray diagrams of the compositions situated along the same line C_7A_5M—C_2AS.

The composition: $2(C_2AS)$, C_7A_5M (or $C_{5.5}A_{3.5}M_{0.5}S$) is not very far from the formula, adopted formerly for the compound C_6A_4MS, but, as opposed to the latter, it seems to be homogeneous and has a higher melting point, although incongruent. The X-ray diagrams of both compounds, the former and the new one, are similar if it is considered that some lines are due to the presence of impurities in C_6A_4MS.

It seems probable, too, that there exists a compound C_3A_2M, whose region of precipitation is situated between those of $C_{12}A_7$, CA, and MgO in the system CaO–Al_2O_3–MgO. Its crystalline form and its optical characteristics do not allow it to be distinguished from C_7A_5M, but the distinction can be made by X-ray examination.

Welch thinks that many compounds, analogous to C_7A_5M and C_3A_2M, resulting from the replacement of MgO by FeO, and Al_2O_3 by Fe_2O_3, are possible and that the structure of these solid solutions is extremely complex.

It must be kept in mind that all those results are only provisional: the existence of C_6A_4MS was doubtful (also that of C_6A_4fS) because the formula could not be arranged in the crystal unit determined for the fibrous material. However, the compositions proposed by Welch do not enter more easily into this same crystal unit. The last word has not been said on the subject.

It is not very satisfying to observe that the commercial high-alumina cements contain some 16 percent of iron oxides, and that it has not been possible, so far, to determine the structural distribution of these oxides. Concerning the question of the compound C_6A_4fS, the formula proposed by Parker does not appear as a real solution.

We have been able, effectively, to observe that a high-alumina cement, made in a non-oxidizing atmosphere and presenting a fibrous structure under the microscope, shows, after oxidizing annealing at temperatures over 1,000 °C, a progressive change of the fibers, and, finally, their disappearance (plate 1). In their place appears a ferrite or an aluminoferrite and CA or C_2AS, according to the conditions of experiment.

On the contrary, if annealing is done below 1,000 °C, always in an oxidizing atmosphere, and for periods long enough to reach the total oxidation of FeO to Fe_2O_3 (with verification by chemical analysis) the fibers are not altered and the X-ray diagram of the annealed compound is practically the same as for the starting compound (plate 1–D).

In conclusion, these results place in doubt the initially proposed formula for the fibrous constituent.

The System $CaO–Al_2O_3–H_2O$ at Different Temperatures. Equilibria Diagrams

Work of Bessey [4]

As far back as 1938, Bessey proposed a representation of the system $CaO–Al_2O_3–H_2O$, based on the work by Lea and Bessey, at 25 °C; in this diagram is represented the stable equilibrium curve[3] of the cubic aluminate C_3AH_6 and, related to this curve, a zone in which are found the metastable equilibrium curves of hexagonal aluminates (curve AB and region BDE, fig. 7).

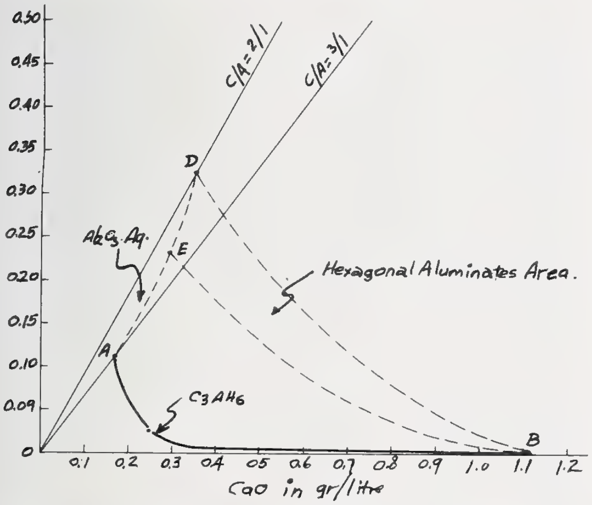

FIGURE 7. *The system* $CaO—Al_2O_3—H_2O$ *at 25 °C.*

After Bessey, 1938 [4].

Work of Wells, Clarke, and McMurdie [59]

In 1943, Wells, Clarke, and McMurdie published a more detailed drawing of the diagram, giving, for temperatures 21 and 90 °C, the equilibrium curves for stable and metastable forms of aluminates, lime, and alumina.

The experimental process chosen by these authors, and adopted afterwards by various investigators for this type of research was the following:

Solutions of monocalcium aluminates are prepared by dissolution of anhydrous CA or high-alumina cement in water, and are mixed with exact quantities of lime water of known concentration. The solution composition is determined at the beginning of the experiments, and the modifications occurring with time are determined by analysis. The precipitates thus obtained from supersaturated solutions are chemically analyzed and studied by various modern investigation processes (such as optical microscopy, electron microscopy, roentgenography, and differential thermal analysis).

Figure 8 indicates a metastable equilibrium curve for hexagonal aluminates, as determined by Wells, Clarke, and McMurdie. On this diagram, the crosses give the starting compositions of solutions, the circles giving the compositions at equilibrium. The dotted lines joining a cross to the corresponding circle give, at any point of the curve, the solution composition at a certain instant. The figures on each line represent the value of the C/A ratio in the precipitate, when in equilibrium with the solution. Wells, Clarke, and McMurdie so determined the curve KRB, which is the metastable equilibrium curve of hexagonal aluminates.

It can be easily seen on the diagram that the increase of CaO concentration in solution is followed by a general decrease of the Al_2O_3 concentration, indicating a progressive increase of the C/A ratio which rises from 2 to 4.

It must be noted that this curve KRB does not present any step for C/A ratios of 2, 3, and 4; this indicates that separate solubility curves for di-, tri-, and tetracalcium aluminates do not exist. The progressive increase can be considered from two different points of view: Either the curve KRB is constituted by the mean solubility values of a series of hydrated aluminates, or the same curve is representative of the solubility of a series of solid solutions, for which the C/A ratio varies. After complementary studies, Wells, Clarke, and McMurdie considered the first hypothesis to be correct.

The same metastable equilibrium curve KRB can be attained by starting from undersaturated

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[3] The expressions "equilibrium curve" or "solubility curve" are indiscriminately used in this text. They always mean that the curves so represented give the composition of the solution at equilibrium with the precipitated phases.

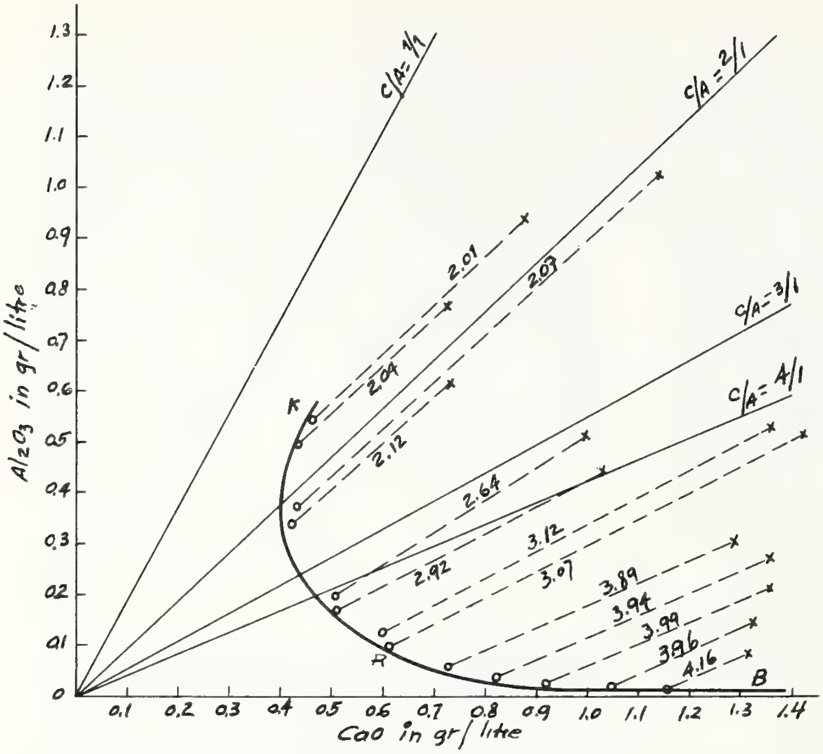

FIGURE 8. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*

Approach to metastable equilibrium for hexagona aluminates (Wells and co-workers [59]).

solutions, instead of supersaturated ones, slowly dissolving pure crystallized aluminates in lime solutions of rising concentrations.

The study, by chemical analysis, of the precipitates formed, and particularly the determination of the H_2O/Al_2O_3 ratio, shows that this ratio rises, generally, with the C/A ratio and that the limits of composition of the hydrated hexagonal aluminates are: $2CaO \cdot Al_2O_3 \cdot 5–9H_2O$ and $4CaO \cdot Al_2O_3 \cdot 12–14H_2O \cdot$

Wells has shown that these hexagonal aluminates are metastable and above 21 °C change more or less rapidly into C_3AH_6. The cubic crystals of C_3AH_6 can be obtained by keeping solutions, whose compositions are the same as the ones already described, for longer times than those allowing the formation of the hexagonal alumi nates. Then, the C/A ratio in the precipitates is very near 3/1 and the equilibrium curve is nearer the coordinates axes. The same curve can be obtained by dissolving C_3AH_6 in lime water.

This solubility curve for C_3AH_6 (A′FB) is represented in figure 9, as well as the mean metastable curve of the hexagonal aluminates. On the diagram are traced the representative lines of the solutions studied, similar to the lines drawn on figure 8, but corresponding only to precipitates in which the C/A ratio is 3/1.

The complete diagram of the equilibria in the system $CaO–Al_2O_3–H_2O$, at 21 °C, as established by Wells, Clarke, and McMurdie, is represented in figure 10. In this system, there are only two stable phases: crystalline gibbsite (AH_3),[4] whose stable equilibrium curve is OF, and cubic tricalcium aluminate (C_3AH_6), whose stable equilibrium curve is BF.

Point F is an invariant stable point for AH_3—C_3AH_6—solution, situated, according to investigators, at Al_2O_3=0.02 g/l and CaO=0.25 to 0.35 g/l. For lime concentrations less than these figures (mean value=0.33 g/l), gibbsite is the stable phase, while C_3AH_6 is stable for values above the same figures.

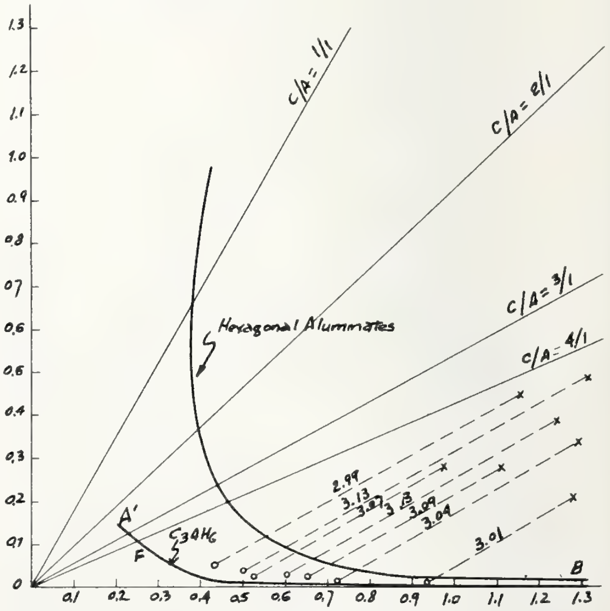

FIGURE 9. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*
Approach to stable equilibrium for C_3AH_6.

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[4] In this text, AH_3 corresponds to perfectly crystallized gibbsite, while $Al_2O_3 \cdot aq.$ is a more or less crystalline form of hydrated alumina.

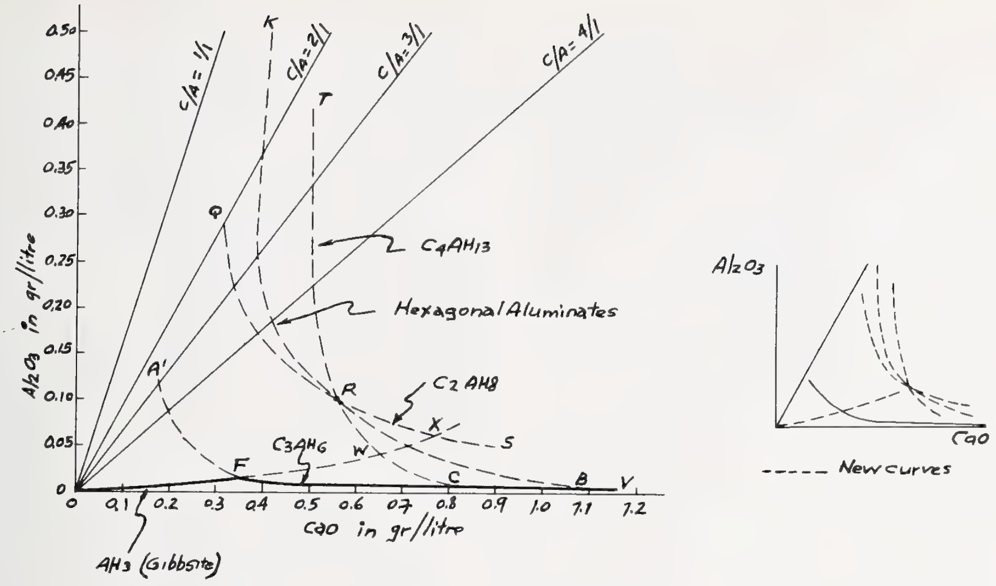

FIGURE 10. *The system* CaO—Al_2O_3—H_2O *at 21 °C.*

After Wells, Clarke, and McMurdie, 1943 [59].

Line FA′ is the metastable prolongation of the curve for C_3AH_6; A′ gives the solubility of gibbsite, as traced by Bessey. It is also the invariant point for Al_2O_3·aq.—C_3AH_6—solution. Normally, in this region of the system, the dissolution of C_3AH_6 should be incongruent, accompanied by precipitation of gibbsite. In fact, it is possible to obtain a congruent dissolution of the cubic aluminate because of the considerable delay observed in the crystallization of alumina gel, the soluble form of this oxide. When looking at the diagram as established by Bessey, it may be seen, indeed, that the curve for Al_2O_3·aq. (OAED) is for its main part metastable towards C_3AH_6.

In figure 10, the curve KRB represents the metastable equilibria of the hexagonal forms of the hydrated calcium aluminates. It was already shown that along this curve, the C/A ratio of precipitates in equilibrium with solution, varies from 2, point K, to 4, point B: this curve has been experimentally established, as shown in the already studied figure 8. For its main part at least, this curve is situated in area BDE, defined by Bessey [4] as the region of existence of the metastable hydrated aluminates, and gives the mean solubility of these compounds.

Although these aluminates seem to be homogeneous, this is only apparent, as shown by X-ray examination. In fact, it seems that there are only two hexagonal compounds, which are able to crystallize together. The examination of the C/A ratios of the precipitates given in figure 8, the values of which vary from 2 to 4, suggests this conclusion.

However, it will be seen further that some investigators think there is a hexagonal tricalcium aluminate, while others suppose that the compound observed is the carboaluminate $C_3A \cdot CaCO_3 \cdot H_n$, whose X-ray diagram is practically the same as that for C_3AH_{12}.

Whatever be the truth, Wells, Clarke, and McMurdie have drawn two metastable equilibrium curves for C_2AH_8 and C_4AH_{13}, respectively QRS and TRV,[5] which envelop the curve KRB.

The point R is the metastable invariant point for C_2AH_8, C_4AH_{13}, and solution. Both hexagonal aluminates coexist at this point, whose coordinates are at 21 °C, CaO=0.53 g/l, Al_2O_3=0.11 g/l.

The point Q indicates the solubility of C_2AH_8 in water, as determined by Bessey.

The solubility curve of C_2AH_8, for rising concentration of CaO, goes from R, invariant point for C_2AH_8—C_4AH_{13}—solution, to point S beyond which C_4AH_{13} is the only relatively stable phase: between R and S, C_2AH_8 is metastable towards C_4AH_{13}.

Curve TRV, the metastable equilibrium curve for C_4AH_n, terminates at point V, the metastable invariant point for C_4AH_n—$Ca(OH)_2$—solution (CaO=1.15 g/l, Al_2O_3=0.0005 g/l).

Those two curves are crossed by the metastable prolongation of curve OF for gibbsite, at two points W and X, hypothetical points which should be, consequently, the two metastable invariant points for AH_3—C_4AH_{13}—solution and AH_3—C_2AH_8—solution, respectively.

Figure 11 illustrates modifications which occur in the system CaO–Al_2O_3–H_2O, when changing temperature from 21 to 90 °C. The only curves concerned are those for C_3AH_6, Al_2O_3·aq. and $Ca(OH)_2$. The curves for hexagonal aluminates are not represented, being very little modified.

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[5] These curves, only theoretical, represent the metastable equilibria of the hexagonal aluminates crystallizing in a pure state.

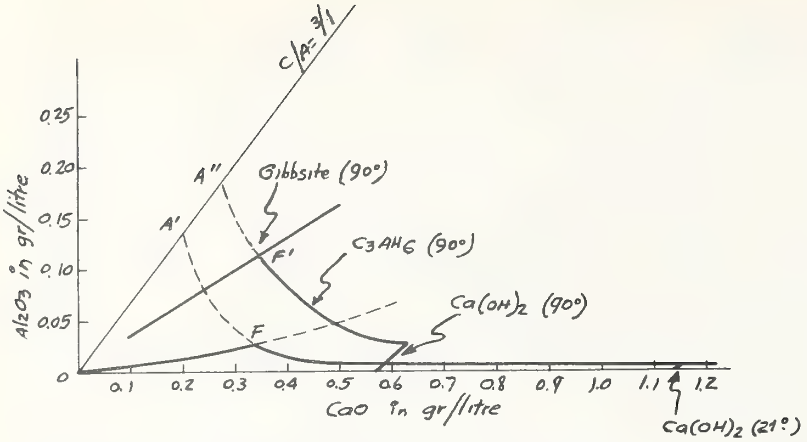

FIGURE 11. *The system* $CaO—Al_2O_3—H_2O$ *at 21 and 90 °C.*

After Wells and collaborators, 1943 [59].

Invariant point F, for $C_3AH_6—AH_3$—solution, which, at 21 °C, has as coordinates $Al_2O_3=0.02$ g/l, $CaO=0.25–0.35$ g/l, is situated, at 90 °C, at $Al_2O_3=0.11$ g/l, $CaO=0.33$ g/l. The curve for AH_3 goes through the origin, but the slope is sharply increased. It will be seen later that stable equilibrium curves for AH_3 are assembled in the form of a sheaf of lines passing through the origin. The stable equilibrium curve for $Ca(OH)_2$ is much nearer the zero and is much longer than at 21 °C.

Work of D'Ans and Eick [17]

More recently, in 1953, the system $CaO–Al_2O_3–H_2O$ was studied again, at 20 °C, by D'Ans and Eick who traced, as did Wells, Clarke, and McMurdie, two distinct metastable equilibrium curves for the two hexagonal aluminates C_2AH_n and C_4AH_n. The diagram (fig. 12) was divided into several crystallization zones, delimited by the different solubility curves.

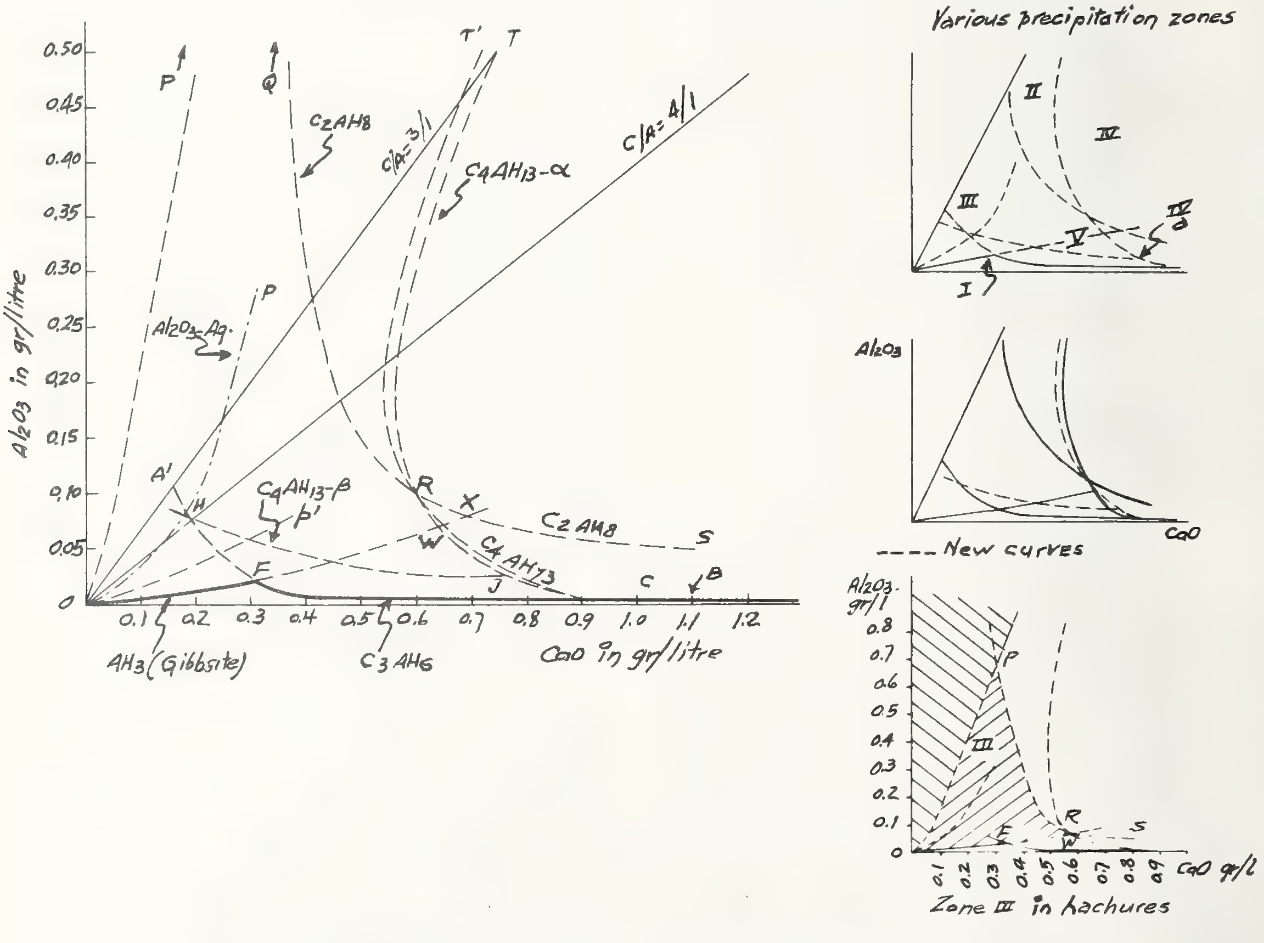

FIGURE 12. *The system* $CaO—Al_2O_3—H_2O$ *at 20 °C.*

After d'Ans and Eick, 1953 [17].

The study made by these authors proceeded quite in the same way as the one by Wells, Clarke, and McMurdie [59], that is to say: Preparation of crystallized precipitates from filtered supersaturated solutions; progressive dissolution of anhydrous or hydrated aluminates in water or in lime solutions of various concentrations; study of the transformation of metastable phases into stable ones by analysis of mother solutions.

Region I is limited by the three stable solubility curves of C_3AH_6, AH_3 (gibbsite), and $Ca(OH)_2$. The solutions whose compositions are situated in this region cannot precipitate, for they are undersaturated towards stable phases in the system.

On the limiting curves of this region, two stable invariant points can be formed. These are F (C_3AH_6—AH_3—solution; $Al_2O_3=0.025$ g/l, $CaO=0.315$ g/l); and B (C_3AH_6—CH—solution; $Al_2O_3=0.00325$ g/l, $CaO=1.172$ g/l).

The stable equilibrium curve C_3AH_6, like the one for gibbsite, was defined by dissolving the pure compound in lime solutions of various concentrations, that is, starting from undersaturation. At ambient temperature, C_3A is dissolved extremely rapidly, while C_3AH_6 is often very slow to precipitate. The supersaturation, in this case, is such that it is possible to enter a region where the supersaturation is very strong towards hexagonal aluminates; then these compounds precipitate first.

Region IV is entirely situated at the right of the limit TRS. Solutions can be obtained whose compositions lie in this zone, by dissolving anhydrous CA or high-alumina cement in water. The filtered solutions when mixed with such quantities of lime water that their C/A ratios lie between 3/2 and the quasi-supersaturation in CaO, precipitate a crystalline phase. The solid composition is not homogeneous. It is a mixture of C_2AH_8, C_3AH_{12}, and for the most part α-C_4AH_{13}, all of them crystallizing as hexagonal plates. It is not possible to distinguish one compound from another except by their refractive indices. The pure compounds, however, are seldom found because of their strong tendency to give mixed crystals.

D'Ans and Eick think that concerning C_3AH_{12}, it is possible to consider this compound as a mixture of C_2AH_8 and α-C_4AH_{13} or C_2AH_8 and lime.

The fact that there is a transition point R ($Al_2O_3=0.095$ g/l, $CaO=0.610$ g/l) makes the hexagonal aluminates of higher lime content than C_2AH_8 metastable towards this last compound for the section of the curve which is above R. On the contrary, compounds corresponding to the portion RS are metastable toward α-C_4AH_{13}.

Besides, although one might expect to see C_2AH_8 precipitate in the region at the right of R, before any other compound, only small quantities of it are observed, and they transform progressively into α-C_4AH_{13}. The formation of this tetracalcium compound and of its mixed crystals with other compounds containing a lower proportion of lime, is consequently faster than formation of C_2AH_8.

Because of the composition variations of hexagonal phases, the tracing of the maximum solubility curve of C_4AH_{13} is somewhat dubious. For this reason, it has been doubled by a curve T′RC which represents the true compositions experimentally obtained at equilibrium. This curve goes through regions II and IVa and is representative of hexagonal aluminates containing a high proportion of α-C_4AH_{13}, and not only the metastable equilibrium curve for this compound. From a practical point of view, T′RC is more significant than TRC.

Region II is situated between the two curves for hexagonal aluminates C_2AH_8 and C_4AH_{13}, and is limited in its lower part by the portion of curve WX, which is situated between the crossing points of both preceding curves with the metastable prolongation of the curve of gibbsite beyond point F. (W:$Al_2O_3=0.065$ g/l, $CaO=0.660$ g/l, and X:$Al_2O_3=0.072$ g/l, $CaO=0.700$ g/l).

It is in this region that the solubility curves for C_3AH_{12} and C_3AH_{18} would be found. The latter crystallizes in the form of needles, mainly from solutions containing little lime. This compound probably would not crystallize in pure form, but would always coprecipitate with other types of solids.

The solutions whose compositions lie in the part of the region II, which is the richest in Al_2O_3, give, in addition to the less metastable aluminates, $Al_2O_3 \cdot aq$. In this region II, it is equally possible to maintain for a while solutions which are undersaturated towards C_4AH_{13}, without precipitation of solid phases. The term undersaturated solution must be understood to mean a solution supersaturated towards a stable phase, but not towards a metastable phase.

The change in composition of the solutions of high Al_2O_3 content occurs, as for solutions poorer in Al_2O_3, in the direction of point R, attaining finally the point W. At the same time, a large quantity of gibbsite precipitates. For this reason the solubility of the most soluble elements may be disturbed in such a way that the solution compositions are displaced, through region III, along the metastable curve for $Al_2O_3 \cdot aq$.

The curve QRX, a limit of region II, is representative of the solubility of pure C_2AH_8.

Region IVa is limited by the portions of curves SX, XW, WC. Starting from supersaturated solutions in the region IV, the precipitate is mainly α-C_4AH_{13}, or more precisely, mixed crystals a little less rich in lime, whose compositions are on the curve T′RC. Thus the region IVa is rapidly crossed.

The case is not the same when starting by dissolution of C_2AH_8 in a lime solution. In this case, a metastable equilibrium is first established between the solution and C_2AH_8, and simultaneously there occurs a fixation of the lime in solution, with as a consequence, a slow change of C_2AH_8 to α-C_4AH_{13}.

The solutions of region IV (WFC) are characterized by a supersaturation towards stable C_3AH_6. However, at 20 °C, this formation of C_3AH_6 is not very abundant. It is necessary to operate at temperatures higher than 30 °C to observe a rapid transformation.

Region III, limited between points P, R, W, F, O, and the ordinate for Al_2O_3 concentrations, contains all the alumina hydrates that are metastable towards gibbsite; the crystallization of this compound has never been completed, either from supersaturated solutions, or by aging of other hydrates in the system.

The curve PRW must be considered consequently as the equilibrium curve of the various alumina hydrates with C_2AH_8, above point R, and with C_4AH_{13} below the same point. The solubility curve for freshly precipitated hydrated alumina is an almost straight line running from the origin to the point P. This last point is the invariant metastable point for $Al_2O_3 \cdot aq.—C_2AH_8—$solution ($Al_2O_3=0.681$ g/l, $CaO=0.324$ g/l).

Alumina gel is able, after aging, to pass slowly to the gibbsite state, the representative curves distributing themselves, as already said, in form of a sheaf between the curve OP, representative of $Al_2O_3 \cdot aq.$, and the curve OF of the perfectly crystallized gibbsite. (In the diagram, figure 12, three of these curves have been represented: OP corresponding to fresh precipitated alumina, and Op and Op′ corresponding to the same hydrated alumina after aging 11 days and 2 months, respectively.)

Finally, D'Ans and Eick observed, in regions V and III, for low-alumina concentrations, large hexagonal plates, tending to form mixed crystals with other hexagonal hydrates. The authors prepared them by reacting hydrated alumina with concentrated lime solutions.

The equilibrium curve JH for β-C_4AH_{13-14} has been drawn by the writers with rather little precision. It begins at point H, intersection with the line for C/A ratio=4/1, crosses the curve for C_3AH_6, and joins, very probably, the curve for α-C_4AH_{13} at point J.

It can be observed that the work by D'Ans and Eick confirms the suppositions and facts expressed or established first by Bessey, later by Wells, Clarke, and McMurdie. The establishment of a new metastable equilibrium curve (HJ) for β-C_4AH_{13-14} is, however, original with these authors.

Work of Peppler and Wells [43]

Peppler and Wells, in 1954, returned to the study of the system Al_2O_3–CaO–H_2O in a very complete way, and for a whole series of temperatures. Besides the study of the system at 21 and 90 °C, which was no more than a revision of the previous research by Wells, Clarke, and McMurdie, the following temperatures were investigated: 50, 120, 150, 200, and 250 °C. Only the temperature of 50 °C has been considered in the following. Its representation is given in figure 13.

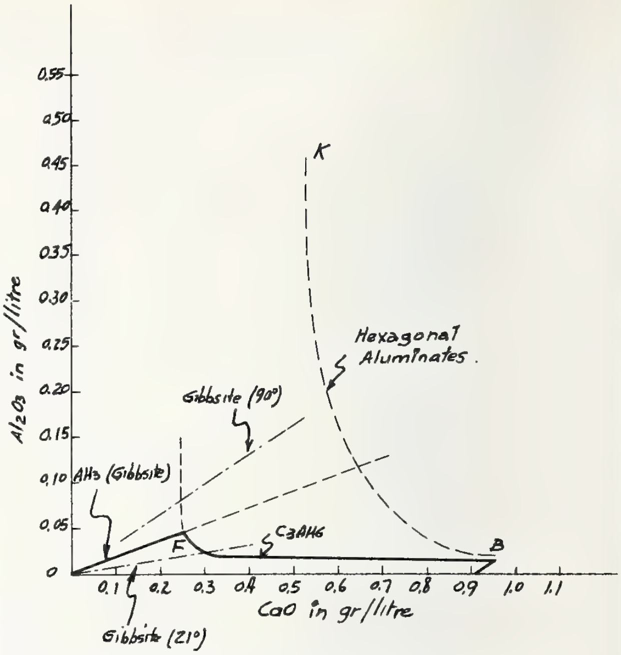

FIGURE 13. *The system* $CaO—Al_2O_3—H_2O$ *at 50 °C.*
After Peppler and Wells, 1954 [43].

Using techniques analogous to those previously described, the authors tried to define the part played by the hexagonal phases in the system at 50 °C. The transformation of the hexagonal phases to the cubic aluminate is faster at 50 °C than at 21 °C. The authors felt, however, that this change was still too slow to permit them to define the exact position of the stable equilibrium curve for C_3AH_6 by starting from supersaturated solutions. This curve has been drawn, consequently, starting from undersaturated solutions; it was thus observed that, as at 21 °C, the cubic hydrate dissolves congruently in lime water, until the concentration corresponds to the invariant point $C_3AH_6—Ca(OH)_2—$solution.

The equilibrium curve for cubic C_3AH_6 at 50 °C presents the same aspect as the curves at 21 or 90 °C, and is situated between these. It is a member of a family of equilibrium curves, as was supposed by Wells, Clarke, and McMurdie.

Point B represents the invariant point $Ca(OH)_2—C_3AH_6—$solution ($CaO=0.961$ g/l, $Al_2O_3=0.005$ g/l).

Gibbsite (AH_3) tends towards its equilibrium curve much more slowly again than C_3AH_6.

It seems probable that alumina gel has a metastable existence at 50 °C, its equilibrium curve being situated above the stable curve of gibbsite (AH_3), crossing first the metastable prolongation of the curve for C_3AH_6 and then the metastable curve for the hexagonal aluminates. The solubility of $Al_2O_3 \cdot aq.$ is a little higher at 50 °C than at 21 °C, gibbsite being the stable form of alumina in the system at 50 °C.

The invariant point C_3AH_6—AH_3—solution is at the intersection of the stable equilibrium curves for the two compounds. An attempt was made to verify its position by dissolving gibbsite and cubic aluminate in water and by analyzing, at regular intervals, the composition of the solution. This was found to be impossible.

The invariant point between the metastable hexagonal phases and the metastable prolongation of the stable curve for gibbsite is situated at: $Al_2O_3=0.130$ g/l, $CaO=0.630$ g/l. This point corresponds fairly well to the point determined at 21 °C.

The solubility of $Ca(OH)_2$ is situated also, as was expected, in an intermediate position between those determined at 21 and 90 °C. The stable equilibrium curve for $Ca(OH)_2$ at 50 °C is, compared to the one determined at 21 °C, nearer the origin and longer.

Figure 14 shows the different positions for the essential curves of the diagram for the system Al_2O_3–CaO–H_2O at various temperatures between 5 and 90 °C. They were established by Buttler, whose work is detailed below, on the basis of data given by Wells, Clarke, and McMurdie [59], Peppler and Wells [43], and Bessey [4] as well as his own results.

All these diagrams are representative of the system Al_2O_3–CaO–H_2O at ambient temperatures or above. The range of temperature between 20 and 0 °C has been quite recently explored, first by Carlson [15] at 1 °C and later by Buttler [11] at 5 °C.

Work of Carlson [15]

The diagram proposed by Carlson, at temperature of 1 °C, is shown on figure 15. The author made the following remarks: The position of the solubility curve for gibbsite (OF) is only approximate. The position of B, solubility of $Ca(OH)_2$, has been fixed from various data found in the literature. The curve RB cannot cross the abscissa axis at point B; thus there must exist, in the vicinity of this last point, an invariant point for an Al_2O_3 concentration of about 0.001 g/l. Between R and this hypothetical invariant point are two curves, the lowest being representative of the stable equilibrium of C_4AH_{13}, the higher being the metastable equilibrium curve for C_2AH_8.

The curve QDR is essentially an "average" curve, experimentally drawn from data obtained by precipitation (supersaturation) and by dissolution (undersaturation).

Curve ED is the metastable equilibrium curve for CAH_{10} and appears for the first time in a diagram representative of the system Al_2O_3–CaO–H_2O. Its position is rather uncertain, because of the dispersion of the experimental results; nothing is known of its prolongation on the left.

This being established, it may be considered that, at 1 °C, the stable phases in the system are AH_3 (gibbsite), C_4AH_{13}, and $Ca(OH)_2$. The position of F, invariant point AH_3—C_4AH_{13}—solution, is ill defined. On the other hand, invariant point B for C_4AH_{13}—$Ca(OH)_2$—solution has the following coordinates; $Al_2O_3=0.001$ g/l, $CaO=1.30$ g/l, thus corresponding fairly well with the solubility value of $Ca(OH)_2$ as given in the literature for this temperature.

The metastable equilibrium curve for C_2AH_8 is QDRB and, on the section RB, practically coincident with the stable equilibrium curve for C_4AH_{13}.

Point D is the metastable invariant point C_2AH_8—CAH_{10}—solution

The metastable solutions whose compositions lie at the right of QD precipitate C_2AH_8; as soon as their initial composition reaches QD, CAH_{10} is formed simultaneously, and the concentration moves towards D.

The solutions of highest lime content precipitate C_2AH_8 and C_4AH_{13} at the same time; as long as C_2AH_8 can precipitate, C_4AH_{13} controls the solution concentration, but as soon as the dical-

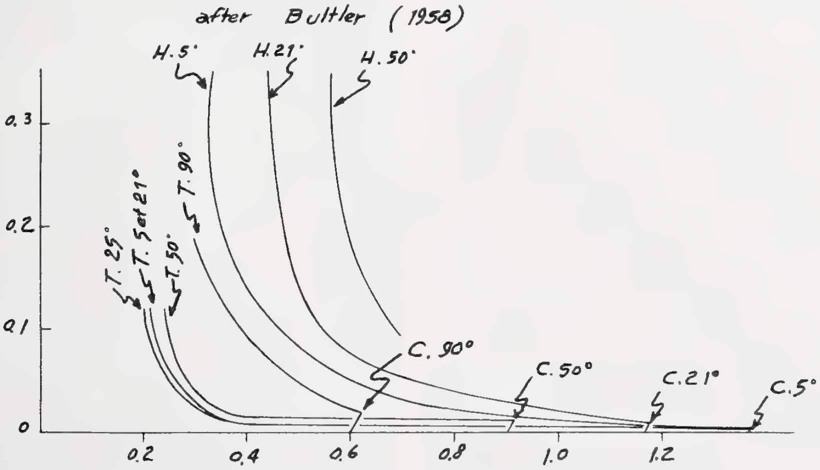

FIGURE 14. *The system* CaO—Al_2O_3—H_2O *at various temperatures.*

Equilibria curves for $Ca(OH)_2$ (curves C); C_3AII_6 (curves T); hexagonal aluminates (curves H).

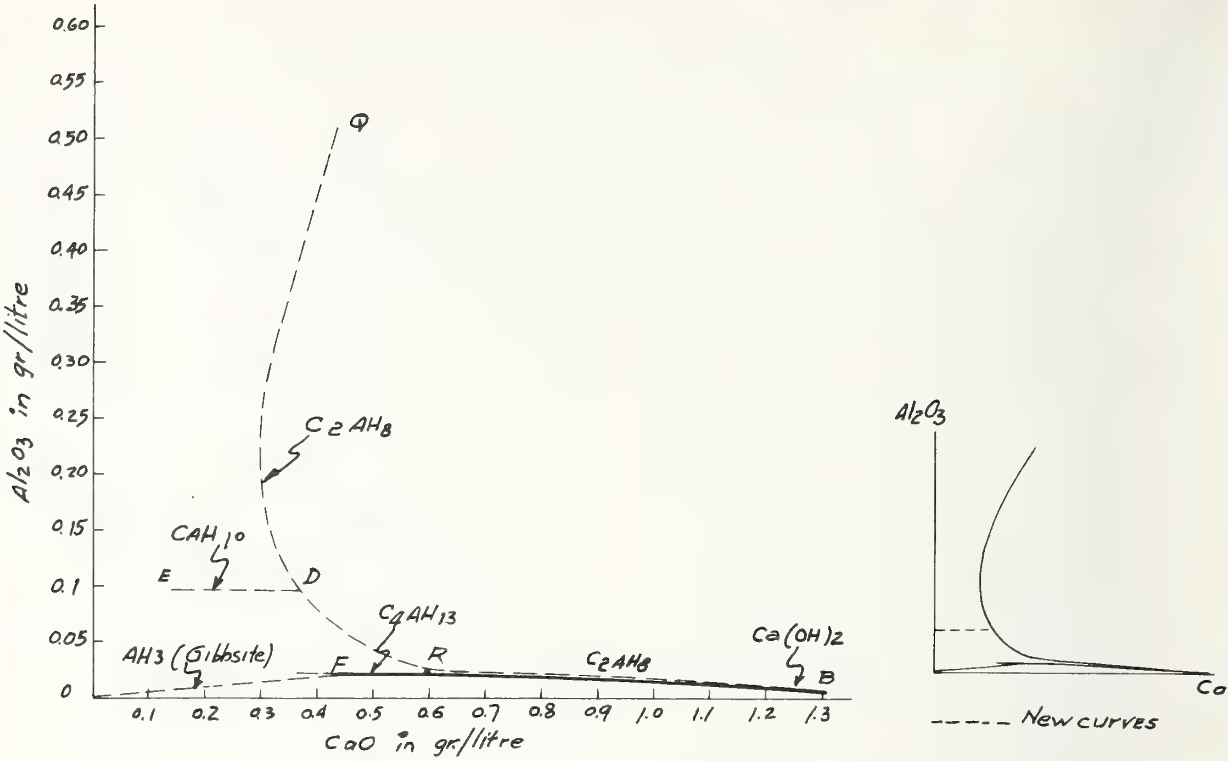

FIGURE 15. *The system* $CaO-Al_2O_3-H_2O$ *at 1 °C.*

After Carlson, 1958 [15].

cium compound is wholly precipitated, the concentration goes from curve DR onto curve FR.

The area enclosed between the abscissa axis and OFRB is representative of stable solutions in the system at this temperature. Above OF, the solutions are metastable towards gibbsite, but the precipitation of this last compound, as already noted, is extremely slow. In region QDE, the solutions precipitate CAH_{10}.

It is interesting to compare this diagram at 1 °C with those traced by Wells and collaborators and by D'Ans and Eick: The diagram at 1 °C is first characterized by the drawing of a metastable equilibrium curve for CAH_{10} which had not yet appeared in previous diagrams. The curve QDRB presents no novel characteristic in comparison with the diagrams at 21 and 90 °C; it always presents a confused section between R and B. However, the diagram for the temperature of 21 °C does not present a stable solubility curve which can be compared to FR. It must be noted that D'Ans and Eick had drawn a solubility curve for β-C_4AH_{13-14} in the immediate vicinity of FR. Another important characteristic of the system $CaO-Al_2O_3-H_2O$ at 1 °C is the lack of a stable equilibrium curve for cubic C_3AH_6.

This remark had been made as far back as 1952, by Longuet [36], in his potentiometric study of calcium aluminate solutions. This writer observed in particular that the solutions of aluminates give a monovalent aluminate ion. This aluminate ion, whatever its origin, gives identical compounds, under analogous conditions. Also, the dissolution of C_3AH_6 in water, followed by evaporation at low temperature, permits the changing of the cubic to the hexagonal form.

Work of Buttler [11]

The diagram of the system $CaO-Al_2O_3-H_2O$ at 5 °C, as established by Buttler, is shown in figure 16. As had been done by D'Ans and Eick [17], Buttler has divided the diagram into various zones of precipitation, limited by the stable and metastable equilibrium curves.

In *Region 1* the solutions precipitate C_4AH_{13}, C_2AH_8, or both compounds simultaneously. It may be verified that when the C/A ratio is higher than 5, C_4AH_{13} precipitates alone, the final concentration of CaO being then 0.53 g/l minimum, while for a C/A ratio between 3 and 5, both hexagonal hydrated compounds, the di- and tetracalcium aluminates, crystallize. In any case, the equilibrium is always rapidly attained.

In *Region 2*, the precipitated solid is most often constituted by two phases, and the equilibrium is difficult to reach; CAH_{10}, C_2AH_8, C_4AH_{13} and Al_2O_3·aq. are formed. In most cases, these four compounds are formed simultaneously, but some of them disappear on aging. The compositions at equilibrium are situated along DQ. For a given total composition (solution + precipitate),

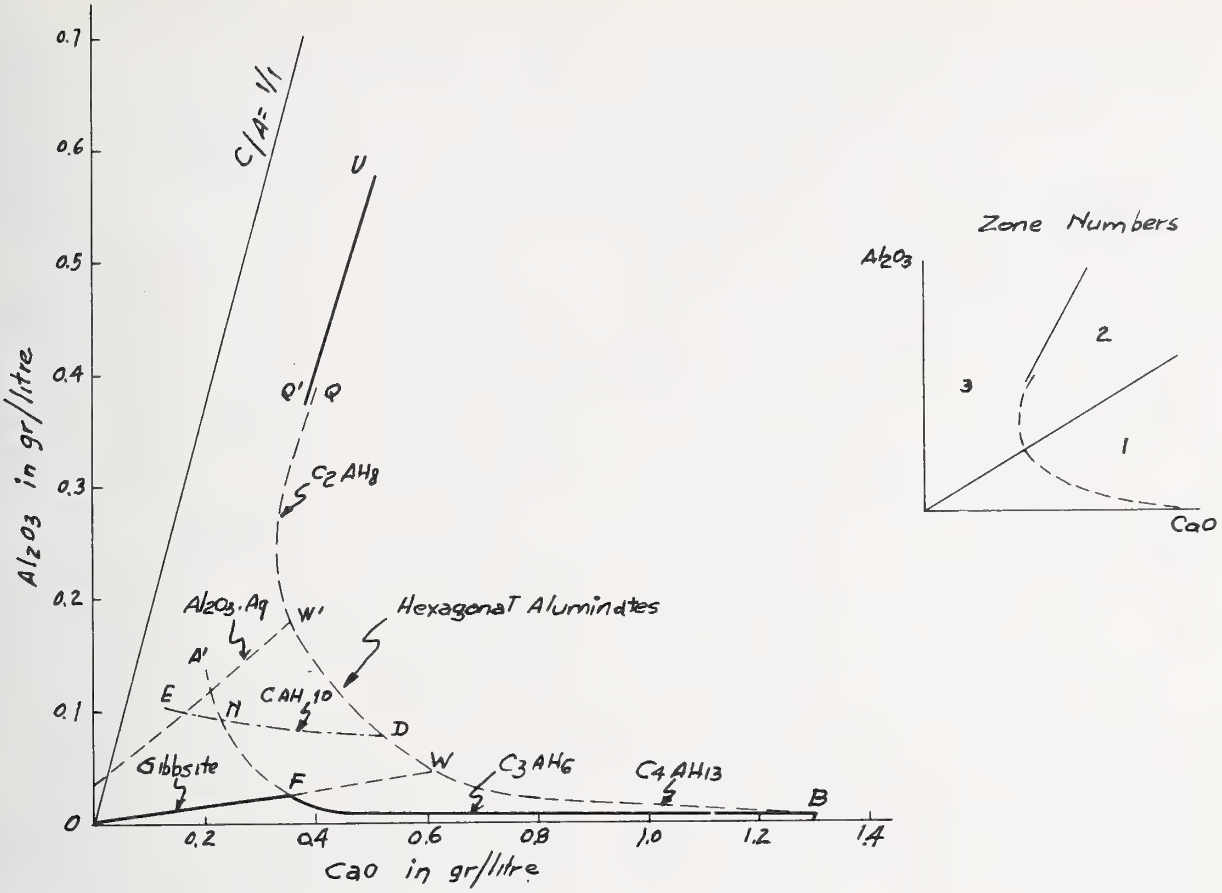

FIGURE 16. *The system* $CaO—Al_2O_3—H_2O$ *at 5 °C.*

After Buttler, 1958 [1].

that of the solution varies with time, running along this curve. It seems that, after a sufficient period of time, the solution composition may go above DQ, the C/A ratio in the solid lessening.

In agreement with the preceding facts, products obtained after a short enough delay have a high content of C_2AH_8 and at the same time contain C_4AH_{13}, while, on the contrary, products obtained after longer delay are frequently rich in CAH_{10} and Al_2O_3·aq.

The product formed essentially in *Region 3* is generally CAH_{10}, often mixed with Al_2O_3·aq., and the solutions at equilibrium possess compositions principally situated to the left of QD and on or above curve ED. The solution concentrations lessen with time and reach a point at least very near ED.

Curve Q′U is in a zone where precipitation of Al_2O_3·aq. occurs; this continues until the solution compositions reach the line Q′U, near point Q. The slope of the line corresponds to a molecular ratio C/A equal to unity. Then CAH_{10} precipitates, the compositions of the solutions varying towards the lower part of the diagram, in the part of region 3 situated above ED. Beyond Q, Al_2O_3·aq. is formed simultaneously with CAH_{10}, alumina tending to predominate. At last, after sufficient time, the solution compositions are stabilized a little above ED, and the precipitates consist of CAH_{10} mixed with ill-crystallized gibbsite.

With total compositions (solution + precipitate) in the vicinity of Q U, traces of C_2AH_8 and C_4AH_{13}, mixed with Al_2O_3·aq. are sometimes observed, and the solution compositions are very near, or on, DQ.

When the lime and alumina concentrations are very low, Al_2O_3· aq. is formed, which is eventually accompanied by CAH_{10}, and the compositions of the solutions are below point E. Al_2O_3·aq. may appear as bayerite (AH).

As the metastable phases persist for long periods, the study of the diagram cannot give much information about the stable phases. However, after the study of the equilibria at higher temperatures, it seems logical to suppose that the stable compounds at 5 °C are always gibbsite and cubic tricalcium aluminate, C_3AH_6. The equilibrium curves of the two compounds are respectively OFW and BFA′; they differ only slightly from the ones drawn at 20, 21, or 25 °C by previous investigators. The portions OF and BF alone are representative of stable equilibria; their prolongation and the other curves in the diagram represent metastable equilibria.

The compounds C_2AH_8 and C_4AH_{13}, both metastable, have, it has been said, very similar crystalline structures, and so it is difficult to trace individual metastable equilibrium curves for these compounds. Curve BWDQ is common to them; on the side of the high CaO concentrations, it corresponds to a metastable equilibrium for C_4AH_{13}; the other end, for high alumina concentrations, corresponding to C_2AH_8.

The triple point C_2AH_8—C_4AH_{13}—solution (R on the other drawings) is very difficult to place with precision; the curve BWDQ appears effectively as a continuous one, and an important section (approximately DW) is common to both hexagonal aluminates. It seems probable that this point is in the vicinity of the point corresponding to the maximum CaO concentration for which the presence of C_2AH_8 is observed. It must be noted that the determination of this triple point is difficult, whatever the temperature.

If C_4AH_{13} and C_2AH_8 are the true metastable phases in the system at 5 °C, it is no less true that the first one has a region where it is relatively stable for CaO concentrations higher than 0.5 g/l; C_2AH_8 is much more transitory. Between certain concentrations, this compound may be more stable than C_4AH_{13}, but it remains always metastable towards CAH_{10}. The latter presents a metastable equilibrium curve ED; its evolution is very slow and for concentrations lower than 0.5 g/l, it is stable towards C_2AH_8 and C_4AH_{13}. For higher concentrations, it reacts with the solution to give C_4AH_{13} and, finally, the stable phases C_3AH_6 and AH_3.

A well-defined solubility curve for $Al_2O_3 \cdot aq.$ cannot be drawn because of the tendency for this compound to crystallize very slowly and poorly. It may be assumed that a whole family of curves corresponding to alumina hydrates is situated above the curve for gibbsite (OFW).

It has been said previously that, at 21 °C, the metastable hexagonal aluminates C_2AH_8 and C_4AH_{13} change rapidly (in about 10 days according to Wells, Clarke, and McMurdie [59]) into the cubic aluminate, C_3AH_6. At 5 °C, it is impossible to pass directly from C_2AH_8 or C_4AH_{13} to C_3AH_6; it is necessary to pass through the intermediary of CAH_{10}, and the transformation is always excessively slow. After 470 days, the author was unable to observe the formation of C_3AH_6 except in 3 experiments among 50, and then in very small quantities.

The compound CAH_{10} is not represented in the diagrams established by Wells, Clarke, and McMurdie, or D'Ans and Eick. Buttler, however, was able to trace its metastable equilibrium curve at 5 °C; AH_3 being never correctly crystallized, a part of this curve (EN) is stable not only towards C_2AH_8 and C_4AH_{13}, but also towards C_3AH_6.

A virtually stable mixture of CAH_{10} and $Al_2O_3 \cdot aq.$ can be obtained as long as the curves for the two compounds cross on the left of point N. But if the crystalline state of $Al_2O_3 \cdot aq.$ is near that of gibbsite, CAH_{10} can dissolve with subsequent precipitation of C_3AH_6.

These two studies of the system $CaO–Al_2O_3–H_2O$ at low temperatures, by Carlson and by Buttler, show, among other interesting data, the reality of a metastable solubility curve for the compound CAH_{10}. The work by Buttler, at 5 °C, confirms the results obtained by Carlson at 1 °C.

Work of Percival and Taylor [44]

The question may be asked if this curve for CAH_{10} can be traced at 21 °C, despite its absence from the diagrams by Bessey [4], Wells, Clarke, and McMurdie [59], D'Ans and Eick [17], and Peppler and Wells [43]. The work by Percival and Taylor, this same year 1958, gives an answer to the question.

The diagram at 21 °C, as it has been proposed by these investigators, is shown in figure 17. It must be noted that it differs from the diagram drawn by Wells, Clarke, and McMurdie [59], only by the tracing of the metastable equilibrium curve ED for CAH_{10} at such a temperature. It is situated much higher than the curves defined by Carlson [15] and Buttler [11], at temperatures of 1 and 5 °C. The authors made the following observations concerning CAH_{10} in the system $CaO–Al_2O_3–H_2O$ at 21 °C: Treated with water or a lime solution whose concentration does not exceed 0.57 g/l, CAH_{10} persists as a principal phase. For concentrations between 0.53 and 0.57 g/l, small quantities of C_2AH_8 or C_4AH_{13}, or both simultaneously, are formed with CAH_{10}. For lime concentrations between 0.13 and 0.40 g/l, the dissolution of CAH_{10} is almost congruent. For concentrations lower than 0.13 g/l, small quantities of $Al_2O_3 \cdot aq.$ are simultaneously precipitated.

Except in the case where CAH_{10} reacts with water, the approach to the curve ED is generally fast. Of the two limiting points of the curve: D is the triple point CAH_{10}—hexagonal aluminates—solution. E is the triple point CAH_{10}—$Al_2O_3 \cdot aq.$—solution.

When CAH_{10} is added to saturated lime solutions, the solution composition moves towards the equilibrium curve BWDQ for the hexagonal aluminates, in accord with the results observed by Wells, Clarke, and McMurdie. The precipitation gives first C_4AH_{19}, and after some time (30–40 days) the formation of C_2AH_8 may be observed, this compound disappearing after another period of time (ca. 190 days), leaving again C_4AH_{19} alone.

Point D was determined after examination of the solution obtained by treatment of CAH_{10} in such proportions that, at equilibrium, not only a mixture of C_2AH_8 and C_4AH_{19} was observed, but the persistence of CAH_{10} as well.

It was not possible to reveal the presence of CAH_{10} in the precipitates obtained from crystallization from supersaturated solutions, probably because the quantities are much too low. But

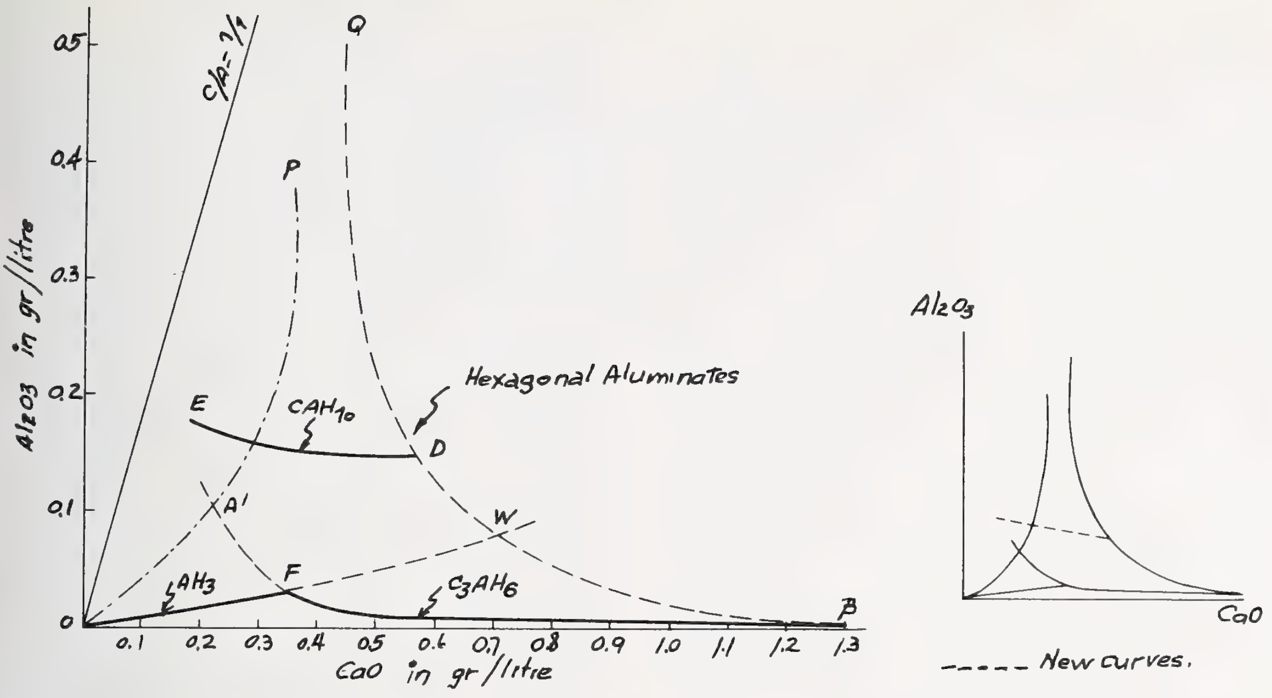

FIGURE 17. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*

After Percival and Taylor, 1958.

the authors think it significant that such a solution approaches curve ED, after a long enough period of time. It seems that by aging of the preparations, these compositions go towards the right side of the diagram, along the line ED. This movement is probably due to the fact that the crystallinity of the hydrated alumina initially formed becomes better with time, and that a certain quantity of CAH_{10} enters into solution.

In these experiments, the writers have not observed any formation of C_3AH_6. However, the observed modification in the solution compositions obtained when starting from CAH_{10} involves the formation of a compound of C/A ratio higher than 1, perhaps C_3AH_6.

Thus, the behavior of supersaturated solutions is somewhat similar to that observed at 5 °C, but at 21 °C the proportions of CAH_{10} formed are less than at the lower temperature. The most notable difference between the systems at 5 and 21 °C is the relative position occupied by the curves ED for CAH_{10} and BFA′ for C_3AH_6: At 5 °C, these two curves cross at a point N (see fig. 16) so that the section NA′ of the metastable prolongation of the curve for C_3AH_6 is metastable towards the section NE of the curve for CAH_{10}. Thus between N and E, CAH_{10} is metastable only towards gibbsite, and, as this crystallizes very slowly, ANE is a region of virtually stable existence for CAH_{10}. On the contrary, at 21 °C, the whole of the curve ED is situated above the curve BFA′ and, in this case, whatever be the lime concentration in the solution, CAH_{10} is always metastable towards C_3AH_6.

As a consequence, it is always possible to observe a transformation of CAH_{10} into cubic tricalcium aluminate, but this eventuality does not involve any knowledge of the speed of this transformation.

These works on equilibrium diagrams well define the regions of stability of the various calcium aluminates. But they do not solve all the problem concerning the respective existences of these compounds. Effectively, they present only a static solution of the problem. To resolve this completely, it would be necessary to consider the kinetic aspect of the transformations. Such a study would be probably very difficult to broach, considering the slowness of the reactions, on which the majority of the investigators agree. This slowness has sometimes forbidden the exact tracing of the equilibrium curves, as, e.g., that for gibbsite, for which, in many cases, it seems implied that it is only a theoretical curve.

The Hydration of Calcium Aluminates and High-Alumina Cements

The studies considered hereafter, made since Steinour's publication [53], concern the hydration of pure calcium aluminates and commercial cements.

These studies are by D'Ans and Eick (1953), Calvet and Longuet (1954), Lea (1956), Wells and Carlson (1956), Farran (1956), Goria and Cussino (1957), Carlson (1958), Buttler (1958), Schippa

(1958), Schneider (1959), and Buttler and Taylor (1959).

It is to be noted that in the following text, data relative to the hydration of C_3A have been systematically excluded, this compound being absent in high-alumina cements.

Work of D'Ans and Eick [17]

This work, published in 1953, is somewhat a continuation (see chapter "Equilibrium diagram") of the investigation by Wells, Clarke, and McMurdie [59]. As in the great majority of such studies the hydration of the aluminates was accomplished with a great excess of water. According to the authors C_2A gives a supersaturated solution, which precipitates very rapidly a mixture of hexagonal aluminates C_2AH_8 and C_4AH_{13} in which C_4AH_{13} is predominant. However, together with the precipitation of C_4AH_{13}, the dissolution of more C_2A occurs, so that the alumina content of the solution rises, and it is C_2AH_8 which finally precipitates. At the same time the dissolution of the anhydrous aluminate is retarded by formation of a superficial film of hydrated compound. As the hydration proceeds, after some days it can be observed that besides C_2AH_8 microcrystalline Al_2O_3·aq. is also produced.

Monocalcium aluminate, CA, gives a supersaturated solution which is much more "stable" than that obtained from C_2A. The precipitation is slower to begin, and the C/A ratio in the crystallized solid has a value of about 1, this ratio being explained by D'Ans and Eick as the result of a simultaneous precipitation of C_2AH_8, C_3AH_{12}, and Al_2O_3·aq. The same retardation of hydration is observed, always due to the formation of a film of hydrated products at the surface of the anhydrous particles.

The investigators' conclusions are that the only aluminates of practical value as hydraulic binders are those whose supersaturated solutions are situated in the region II of their diagram (see fig. 12), the region of highest alumina content, and not in region IV. These compounds give metastable solutions, precipitating slowly, a fact which explains the lack of rapid setting.

D'Ans and Eick also studied the hydration of a commercial high-alumina cement in which the C/A ratio was about 1/1. This cement exhibited almost the same behavior as anhydrous CA, slight modifications appearing possibly because of the presence of secondary constituents: the dissolution of the cement was delayed because of the formation of a gel of silica on the surface of the particles and perhaps, too, because iron hydroxide was formed by hydration of C_4AF, as explained by Brocard [7].

The hydration of high-alumina cement with an excess of water leads, therefore, essentially to the formation of C_2AH_8 and Al_2O_3·aq. (see Koyanagi [27]). D'Ans and Eick remark that neither α-C_4AH_{13} nor C_3AH_6 is formed at 20 °C. The transformation of the precipitates into cubic aluminate is possible, however, at temperatures as low as 30 °C, and the cement then loses a part of its mechanical resistance (see Seailles [52]).

The writers do not agree with Koyanagi, who thinks that the rapid setting of a high-alumina cement is due to the formation of C_3AH_6: they consider highly improbable the idea that such a phenomenon may be attributed to the formation of crystals with a very compact, almost spherical structure, especially when the formation of the said crystals is very slow.

Work of Calvet and Longuet [13]

In 1954, these investigators applied a microcalorimetric method to the study of the hydration of calcium aluminates, which would permit a survey of the thermokinetic aspects of the phenomena. They thus verified Le Chatelier's hypothesis, according to which a saturated solution of anhydrous product is formed first, before a less soluble hydrate may precipitate from the solution which is rapidly supersaturated towards this hydrated compound. They observed also that the crystallization of hydrated phases is complicated by hydrolysis phenomena, indicated by a higher evolution of heat than that observed in crystallization alone.

Moreover, the following observations were made by Calvet and Longuet: The anhydrous compound $C_{12}A_7$ (or C_5A_3) seems to have an important action in the control of the formation of the final hydrated phase. In dilute solutions, it seems that a strong hydrolysis is necessary to form the cubic hydrated aluminate.

Lea's Opinion [32]

Lea [32] examined a number of the various investigators' works, made between the years 1930–1950, and summarized his opinions in his book published in 1956: $C_{12}A_7$ (or C_5A_3) reacts very rapidly with an excess of water to give simultaneously hydrated aluminates and hydrated alumina. CA reacts less rapidly. CA_2 is practically inert.

Whatever the anhydrous compound, at relatively low temperatures under 15–20 °C it tends first to give CA·aq, but, as the temperature rises, it also forms C_2A·aq. It seems probable that, in a general way, the tendency for an anhydrous aluminate to give CA·aq. is less marked when its C/A ratio is low. On the other hand, the transformation of hexagonal aluminates into cubic C_3AH_6 is accelerated by raising the temperature and, besides this factor, is more rapid when the C/A ratio in the anhydrous compound is high.

Work of Wells and Carlson [58]

An extensive study of the hydration of pure calcium aluminates and high-alumina cements was published in 1956 by Wells and Carlson.

Hydration of Pure Aluminates

The investigators studied the behavior during hydration of the three anhydrous compounds C_3A_5, CA, and C_5A_3. They observed that, in spite of their differences of composition, the three aluminates reacted in a very similar way with an excess of water. The resulting solutions reached, in every case, a C/A ratio of about 1/1. The maximum concentration was reached after times which varied with the starting compound. In the same way, the drop of concentration, due to the precipitation of solid phases, varied with the C/A ratio of the anhydrous compound. The drop was slower for CA than for the others.

Figure 18 gives the compositions of the solutions obtained with the three anhydrous compounds. At point a (CaO=0.5 g/l, Al_2O_3=0.6 g/l) the precipitation was, in a general way, very slow. The section ab on the curve is almost vertical, indicating a precipitation of alumina without variation of lime concentration. At point b, the *p*H of the solutions was 11.7–11.8, and the precipitated solids had C/A ratios a little less than 1/1. Under the microscope, the following phases could be distinguished: A hexagonal phase, the authors supposed to be C_2AH_n (and not C_3AH_n as was formerly thought); an amorphous phase apparently colloidal that the authors supposed to be Al_2O_3·aq.; in weak quantities, and accessorily, cubic crystals of C_3AH_6; and calcite probably formed by carbonation of the solid phases.

The hydration, with an excess of water, of the pure calcium aluminates would consequently be essentially characterized by the formation of C_2AH_8 and Al_2O_3·aq., as previously reported by D'Ans and Eick. Wells and Carlson think, as do Assarsson [2, 3], Forsen [21], and Hedin [25], that the dissolution of anhydrous aluminates in water proceeds first without hydrolysis. This occurs later with subsequent precipitation of Al_2O_3·aq., the quantities formed of this last compound varying with the composition of the anhydrous aluminate. The hydrated alumina being only partially soluble, a slight excess of lime is formed which tends to stop the hydrolysis. The immediate consequence is that the C/A molecular ratio of the aqueous aluminate solution, although situated in the vicinity of 1/1, is, in fact, a little higher than this value. In the experiments by Wells and Carlson, the C/A ratio in the precipitates was about 0.66, corresponding roughly to the formation of 2 moles of Al_2O_3·aq. to 1 mole of C_2A·aq.

A phenomenon which all investigators have noted is the marked persistence of solid phases in a metastable state. Besides the aluminates, whose transformations are very slow, alumina, which is one of the two true stable phases of the system Al_2O_3—CaO—H_2O, goes very slowly towards its final form, gibbsite. After a sufficient period of time, a microcrystalline alumina is formed which is an intermediary form between freshly precipitated gel and perfectly crystallized gibbsite. This very slow crystallization of alumina must, according to Wells and Carlson, exert a very important influence on the evolution of aluminates towards their final stable state.

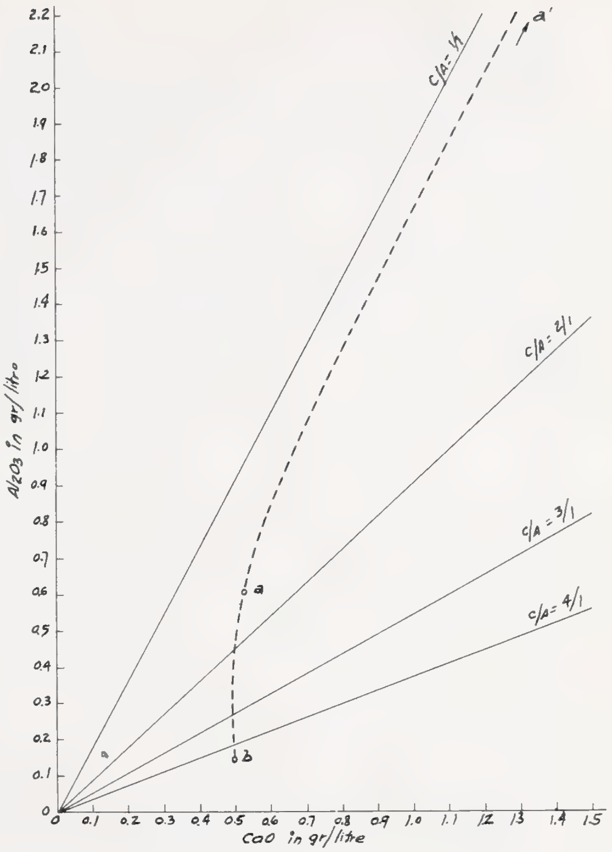

FIGURE 18. *Compositions of solutions formed by action of water on anhydrous aluminates.*

After Wells and Carlson [58].

In figure 19, the lined region contains the compositions of aluminates formed during setting and hardening of pure aluminates. This area covers, as may be seen, the highest part (corresponding to C_2AH_8) of the hexagonal-aluminate curve as defined by Wells, Clarke, and McMurdie. Wells and Carlson consider that in this zone the approach to final equilibrium proceeds by successive steps, for which the reaction velocities differ: first a metastable equilibrium is rapidly established, indicated by point b (hexagonal aluminates), and then those compounds are transformed, by a slower reaction, into compositions indicated by point F (AH_3—C_3AH_6—solution). It may be observed that the solubility curve for lime is situated far from this region, explaining the absence of this compound in high-alumina-cement hydration products.

It is a universally accepted opinion that the transformation of hydrated aluminates into cubic C_3AH_6 in concretes and mortars cured in damp atmosphere at temperatures above 35 °C is respon-

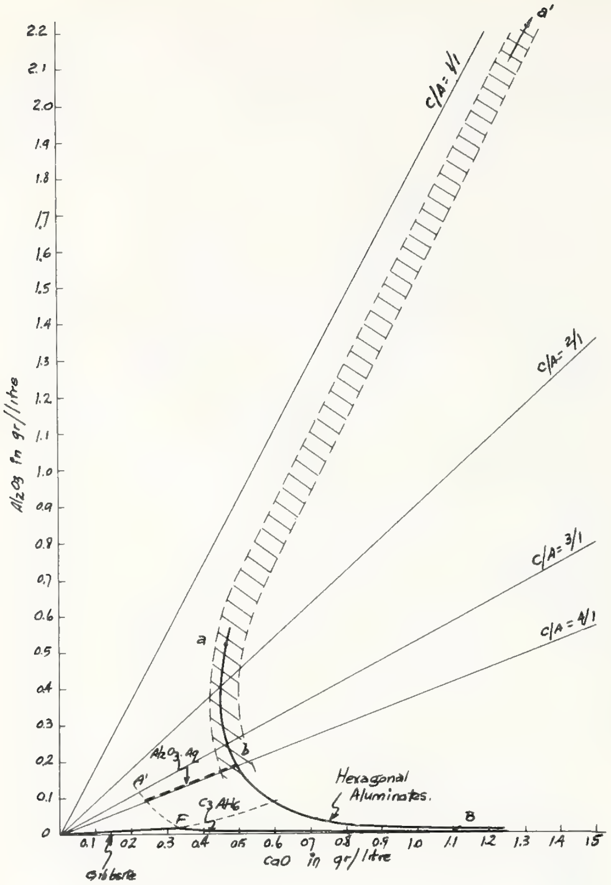

FIGURE 19. *Region in which the setting of high-alumina cements occurs, compared with the system* CaO—Al_2O_3—H_2O.

After Wells and Carlson [58].

sible for the observed loss of mechanical properties. Wells and Carlson agree, but observe that at 21 °C, at which temperature their experiments were conducted, this transformation is extremely slow.

Thus, in a general way, the evolution of the immediate hydration products of aluminates towards the two stable phases in the system Al_2O_3–CaO–H_2O, viz., the compounds C_3AH_6 and crystalline AH_3, is, at normal temperature, extremely slow.

Besides this low reaction speed, which is in favor of the high-alumina cements, another interesting factor must be considered, according to Wells and Carlson: Alumina formed during hydration, more or less in the form of a gel, has adhesive properties common to every kind of gel and acts in a certain sense as an "inorganic adhesive." Its contribution to the mechanical qualities of the hydraulic binder is not negligible.

Hydration of High-Alumina Cements

After their study on pure calcium aluminates, Wells and Carlson repeated their experiments with commercial aluminous cements, to make comparison. Their results were very similar to those obtained with isolated aluminates.

In a general manner, an aluminous binder treated with a large excess of water reacts rapidly to give, without consideration of its composition, a solution in which the C/A ratio is about 1/1, and the *p*H has a mean value of 11.25. Point a, of figure 19, is thus rapidly reached. Later, the solid phases precipitate, the separation of solid phases slackening with time. Point b, on figure 19, is thus slowly reached, and the *p*H at this point is about 11.75.

In this case, the precipitated solid phases are the same as those observed during hydration of aluminates; namely, (1) a phase crystallizing in hexagonal plates, often assembled in spherolites, thought to be C_2AH_8, (2) an amorphous phase, apparently colloidal, or at least not highly crystalline, whose optical properties are those of gibbsite, (3) cubic C_3AH_6, in small quantities, and (4) calcite, always in very small quantities.

Thus, in the presence of an excess of water (and it is necessary to emphasize this point) the commercial high-alumina cements, like the various calcium aluminates, give after hydration a hexagonal phase which is essentially C_2AH_8, and (or almost) simultaneously, a colloidal precipitate of Al_2O_3·aq.

To observe what occurs when these cements are hydrated in presence of an amount of water corresponding to the quantity used in practice, Wells and Carlson performed experiments on neat cements (W/C=0.38) at various temperatures, but above the normal (24, 35, 50, and 80 °C).

The experiments were made on three samples of different commercial cements; the results in table 1 correspond to a hydration of 7 days.

TABLE 1. *Solid phases present in hydrated high-alumina cements, as determined by X-ray diffraction*

Based on work of Wells and Carlson [58]

Observed solid phase	Number of samples (among the 3 examined) showing the observed phase at hydration temperature of:			
	24 °C	35 °C	50 °C	80 °C
Cubic C_3AH_6	None	1 (traces)	2	3
C_2A·aq. (10.6 and 5.3 A) [a]	2 (traces)	3		
CA·aq. (14.6 and 7.3 A) [a]	3 (predominating phase).			
Phase "x" (unknown composition [b]).	2 (predominating phase).	2 (predominating phase).		
Phase "y" (12.5 and 6.85 A *but* very weak lines). [a]		3	3	
Phase "g" (4.85 A) [a] (probably gibbsite).		2 (small quantities).	3	3

[a] Characteristic lines in the X-ray pattern.

[b] Probably CA·$CaCO_3$·H_n, Carlson [15] and Schippa [50].

The complete observations made by the authors are as follows:

(1) After 7 days, the hydration was still incomplete.

(2) The cements which, in the anhydrous state, presented the lines of gehlenite (C_2AS) presented

those same lines after 7 days hydration because of the well-known hydraulic inertness of this compound.

(3) At 24 °C, essentially CA·aq. was formed.

(4) At 35 °C, C_2A·aq. was formed essentially with two other phases, one of them, at least, being a hydrated calcium aluminate.

(5) At higher temperature C_3AH_6 was formed in quantities becoming larger with increased temperature, simultaneously with an ill-defined phase which was probably gibbsite.

(6) The various cements observed, in spite of their different compositions in the anhydrous state, all showed almost identical behavior, confirming the observations with pure aluminates in presence of an excess of water.

Work of Farran [19]

This author attempted as much as possible to make experiments in conditions analogous to those practiced in the preparation of high-alumina-cement concretes and mortars.

According to his results, the aggregates used may have a different influence on the composition of hydrated phases, at least in their immediate vicinity, according to whether they are active or inert. With inert aggregates, and around them, Farran observed the formation of an interfacial film presenting, at least at the beginning, the appearance of a gel, but which later precipitated a phase of hexagonal symmetry, that is to say CA·aq. Finely crystallized alumina was also formed. Under some conditions of experiment, assuming locally an excess of water, e.g., immersion in water of fissured prisms, C_2A·aq. was formed, as observed before by Lafuma [30] and by Wells and Carlson [58] who always obtained this compound in the presence of an excess of water.

Working with an active aggregate, e.g., calcite which may react with the cement paste, Farran observed that the interfacial film was constituted by a crystalline phase, of which the X-ray diagram showed essential lines at: 14.6, 7.7, 7.3, and 3.8 A. According to the author, the lines at 14.6 and 7.3 A are characteristic of CAH_n, while those at 7.7 and 3.8 A are characteristic of a solid solution of carboaluminate $C_3A \cdot CaCO_3 \cdot H_n$ in C_4AH_{13}, a solid solution, whose existence was presumed by Assarsson [3] and Bessey [4].

Work of Goria and Cussino [23]

These two investigators think, as did Lafuma [31] that the formation of cubic aluminate during long periods of curing can be avoided by adding to high-alumina cement a certain proportion of pozzolan which fixes, in the form of a calcium silicate, the lime bound to alumina, this last compound being simultaneously liberated. Goria and Cussino think that under these conditions the formation of cubic C_3AH_6 is partially prevented. The loss of mechanical characteristics would be 10 percent less than that observed when no pozzolan is added to the aluminous binder.

Work of Carlson [15]

It has been previously mentioned that Carlson studied the system Al_2O_3–CaO–H_2O at 1 °C. According to this author, at this temperature, the solid phase which precipitates is CAH_{10}; however, he thinks it possible that C_2AH_8 is formed first but is almost immediately transformed into CAH_{10}. Carlson believes that at 24 °C as at 1 °C, CAH_{10} constitutes the main crystalline phase when the hydration is made with a normal amount of water and not in the presence of an excess. He supposes too that the carboaluminate has a great importance in the process of hydration, for it is impossible to avoid its formation. He thinks, however, that this compound does not form, at least at 1 °C, a solid solution with C_4AH_{13}, as was supposed by Farran [19].

Work of Buttler [11]

In his thesis, in 1958, this author studied the behavior, during hydration, of a high-alumina cement without iron, essentially constituted of CA and CA_2 in roughly equal parts. For comparison, he observed the hydration of CA and CA_2, considered separately. He found that:

(1) CA, at 5 °C, reacts vigorously with water and dissolves almost congruently, at the start of the reaction at least. The solutions thus obtained finally precipitate CAH_{10} and Al_2O_3·aq.

(2) CA_2 behaves differently. During the initial period of hydration no reaction can be observed, but later it starts and accelerates with time, while the CaO and Al_2O_3 contents of the solution rise. The solid finally precipitated is essentially Al_2O_3·aq.

(3) The industrial mixture of CA and CA_2 in reacting with water gave supersaturated solutions which precipitated CAH_{10} and Al_2O_3·aq. Formation of C_2AH_8 was scarcely observed.

Bayerite (AH) may sometimes be formed, instead of gibbsite (AH_3) but simultaneously with calcite. This observation confirms a general opinion, according to which bayerite is formed preferentially to gibbsite if small quantities of CO_2 ions are present.

Thus it may be seen that CA reacts with water more rapidly than CA_2. It is consequently sure that the rapid rising of the CaO and Al_2O_3 concentrations in the solutions obtained from this mixture of $CA+CA_2$ is essentially due to the CA content of the said mixture. The fall of the concentrations, later observed, is due to the CA_2 content of the mixture, but it is possible that the alkalies eventually present play a part in the process.

Buttler observed that the hydrate mainly formed at low temperatures is CAH_{10}. Its transformation into C_3AH_6 is not easy nor rapid, except if the temperature rises, and he was not able, in his experiments at 5 °C, to observe the transformation.

At 21 °C, Buttler also observed that the mixture $CA+CA_2$, and CA alone reacts very rapidly, but that the solution obtained with cement precipitates more rapidly than that obtained with CA alone.

The compound CA_2 reacts very slowly at this temperature also, and the supersaturated solution obtained lets precipitate a solid whose composition is very near the composition indicated by the hexagonal-aluminates curve, while with CA or $CA+CA_2$ the only hydration products seem to be CAH_{10} and Al_2O_3·aq.

At 25 °C, on the contrary, the mixture $CA+CA_2$ leads to the formation of C_2AH_8, concurrently with CAH_{10} and Al_2O_3·aq. This reaction has already been observed by Carlson [15].

Work of Schippa [50]

This author studied the hydration of aluminous cements gaged in the form of neat pastes (W/C =0.4) and cured in damp atmosphere at 15–20 °C. The X-ray examination of prisms showed him that the crystalline phases present were CAH_{10}, $C_3A \cdot CaCO_3 \cdot H_{11}$ and, in some cases, C_3AH_6. Schippa supposes the "phase x" described by Wells and Carlson [58] to be the carboaluminate. He was unable to observe, with sufficient certainty, the presence of C_2AH_8.

Schippa thinks that the influence of carboaluminate formation on the hydration of pure aluminates or high-alumina cements is of first importance and that some uncertainties could disappear as a result of a study of the system Al_2O_3–CaO-CO_2–H_2O.

Work of Schneider [51]

This author's work was primarily intended to find a possible relation between physical property changes and structure modifications. He used for this purpose differential-thermal-analysis techniques. He believes that CAH_{10} is the only aluminate which is formed during hydration of high-alumina cements at ambient temperature. Raising the temperature leads to the formation of C_3AH_6 and AH_3, by way of a reaction that Schneider thinks to be of a hydrothermal sort: water coming from dehydration of a part of the CAH_{10} could react with the remainder of this compound, already partially dissociated. This author believes that the loss of mechanical strength of high-alumina-cement concretes is perhaps due to the tensions provoked by the loss of water when the prisms are heated, and not only to the nature of the aluminates formed at higher temperatures than the ambient.

Work of Buttler and Taylor [12]

Both authors came back to the study of hydration of CA and CA_2 in normal gaging conditions, which compounds, as was seen, had been the subjects of researches by Buttler in his thesis of 1958. It is now certain that separately CA reacts with water more rapidly than CA_2. However, in the case of a mixture of $CA+CA_2$, which is realized in the cement industry, the reaction of CA with water adds lime to the solution, and then the CA_2 reacts more rapidly.

The authors have recognized that the only hydration products present at 5°C are CAH_{10} and Al_2O_3·aq. At this temperature, they have not observed the formation of C_3AH_6. With an excess of water, CA and CA_2 give solutions which precipitate only Al_2O_3·aq.

During the past few years, the opinion seems to be unanimous concerning the hydration process for calcium aluminates and high-alumina cements. The action of temperature during the hydration seems to be highly important. It determines the nature of the hydrated aluminates obtained. It is interesting to note that hexagonal dicalcium aluminate, C_2AH_8, which had always been considered as the chief compound of the hydration products at ordinary temperature, is only very transitory, at least when the amount of hydration water corresponds to that used in the preparation of concretes and mortars. On the other hand, this compound is preferentially formed in the presence of a great excess of water.

Hexagonal Tricalcium Aluminate and Carboaluminate

The reality of the existence of hexahydrated tricalcium aluminate, C_3AH_6, of hydrated monocalcium aluminate CAH_{10}, and of both hexagonal hydrated di- and tetracalcium aluminates, C_2AH_8 and C_4AH_{13}, is well established. But a doubt always remains concerning the reality of a hexagonal hydrated tricalcium aluminate, C_3AH_{12}, as well as the existence of a tricalcium aluminate crystallizing as pseudo-hexagonal needles, C_3AH_{18-21}.

In the diagram by Wells, Clarke, and McMurdie [59], an equilibrium curve for hexagonal aluminates is drawn: along this curve, precipitates are in equilibrium with the solutions of aluminates whose compositions, at least at the beginning, are situated on the right of the curve, and show C/A ratios varying continuously from 2 to 4, C_2AH_8 and C_4AH_{13} being the extreme members of the series. Wells, Clarke, and McMurdie first attempted, as indicated in a preceding chapter, to replace the previous curve by two others representing respectively the equilibria for C_2AH_8 and C_4AH_{13}. The study by D'Ans and Eick has shown that these equilibrium curves are purely theoretical and that the compositions of the solids instead of corresponding, for example, to C_4AH_{13}, correspond in fact to compounds with less lime (see fig. 10 and 12).

The curve was considered, later, a unique curve whose higher part represents the metastable equilibrium for which C_2AH_8 is largely predominant, while the lower part corresponds to compositions in which C_4AH_{13} is more abundant. The middle part, however, remains vague. It seems to correspond to an overlapping of the two curves of di- and tetracalcium aluminates, which are practically the prolongation one of the other and must present a metastable invariant point C_2AH_8–C_4AH_{13}–solution which has never been determined with precision.

Other investigators trusted in the reality of a hexagonal compound C_3AH_n and like Wells, Clark, and McMurdie, gave preparation methods, optical characteristics, and dehydration curves. Among them were, before 1950, Assarsson [2], Lefol [33], and Travers and Sehnoutka [55]. In 1952, Koyanagi [28] obtained hexagonal plates whose composition corresponded to the formula $C_3AH_{10.5}$. The same year, Longuet [36], preparing C_3AH_6 by various methods, always obtained this compound mixed with more or less important quantities of C_3AH_{12}, recognized by X-ray examination.

D'Ans and Eick [17], in 1954, also noted the existence of C_3AH_{12} and acicular C_3AH_{18-21}, whose metastable equilibrium curves would be situated in the region between the two curves drawn for C_2AH_8 and C_4AH_{13}. However, they presumed that the existence of tricalcium aluminates with 12 or 18–21 moles of water, was much more transitory than that of C_2AH_8 or C_4AH_{13}. The compounds C_3AH_{12} and C_3AH_{18-21} could be transformed rapidly into di- and tetracalcium aluminates and alumina, their transformation velocity depending on the initial concentrations of the solution from which they precipitate.

In 1956, Brocard [10] asserted again that a hexagonal tricalcium aluminate really exists and that it may be obtained by hydration of C_3A. Around the same period, Govoroff [24] published a short study of the behavior on heating of three hexagonal aluminates. The differential thermal analysis and X-ray examinations show, according to this author, that by simple heating to 80 °C, a mixture of C_4AH_n, C_3AH_{12}, and C_2AH_7 is transformed into C_3AH_{12}, almost in a pure state, whose X-ray diagram presents one essential line at 7.65 A, while the diagram of the initial mixture presents three essential lines at 8.33, 7.65, and 10.6 A, in other words the lines of the three compounds. On the other hand, as soon as the results were published which led them to a publication of their conception of the equilibria diagram of the system Al_2O_3–CaO–H_2O, Wells, Clarke, and McMurdie [59] adopted a position opposed to the reality of a hexagonal tricalcium aluminate.

In the middle part of the curve, for which the C/A ratio in the precipitates at equilibrium is around 3, it may be thought that there occurs either a metastable equilibrium for a hexagonal hydrated tricalcium aluminate or an intercrystallization, in the solid phase, of C_2AH_8 and C_4AH_{13}. Those precipitates have been subjected to X-ray determination, and a diagram has been established.

Actually three theses are opposed, each one having its supporters:

(1) A hexagonal tricalcium aluminate C_3AH_n (n varying from 6 to 21) really exists, the established diagram corresponding to it.

(2) The C_3AH_n does not really exist but is an equimolecular mixture of C_2AH_8 and C_4AH_{13}, obtained by syncrystallization.

(3) The X-ray diagram assigned to C_3AH_n, pertains in fact to a carboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$.

Hypothesis of a Hexagonal Hydrated Tricalcium Aluminated

The X-ray diagram of hexagonal tricalcium aluminate has been published by Thorvaldson, Grace, and Vigfusson [54], Bunn and Clark [6], and Brocard [7]. The essential lines are noted in table 2.

TABLE 2. $3CaO{\cdot}Al_2O_3{\cdot}12H_2O$ (*d* in A)

Thorvaldson and coll. (1929)	Bunn and Clark (1938)	Brocard (1948)
----	7. 70	7. 65
----	3. 77	3. 77
----	----	----
2. 86	2. 85	2. 86
2. 47	----	----
1. 65	----	----
1. 43	----	----

The diagrams established by Bunn and Clark and by Brocard are practically coincident. The one established by Thorvaldson, Grace, and Vigfusson has been realized only for $2\theta = 30$–$90°$ where the aluminates offer no more than the weakest lines, the most intense lines being situated beyond the limits of these angles.

Hypothesis of a Syncrystallization of Di- and Tetracalcium Aluminates

For Wells, Clarke, and McMurdie [59], there would not be a definite compound, but a compound resulting from a syncrystallization of both hexagonal aluminates C_2AH_8 and C_4AH_{13}, in equimolecular proportions. Their arguments are based on the examination of X-ray diagrams for both compounds, whose essential lines are 10.6 A for C_2AH_8 and 8.2 A for C_4AH_{13}.

Wells, Clarke, and McMurdie observed that the precipitates for which the C/A ratio is between 2 and 4 always present strong lines at 10.6 and 8.2 A, the relative intensities depending on the proportions of both aluminates in the "mixture." As these hydrates have structures quite similar parallel to the *a* axis, they are able to syncrystallize in thin successive layers, in so inextricable a way that a refractive index may be observed which is the average value of the indices of both compounds considered separately.

In 1951, Steinour [53] in his general report on aluminates reviewed again the published results and was inclined to accept the hypothesis advanced by Wells, Clarke, and McMurdie, the proofs of the existence of hexagonal C_3AH_n appearing dubious.

In 1954, Peppler and Wells [43] wrote that the X-ray examinations made by Wells, Clarke, and McMurdie, led to the conclusion that there does not exist a hexagonal tricalcium aluminate. Again, Bogue [5] remarks that on the equilibrium curve for hexagonal aluminates, as defined by Wells, Clarke, and McMurdie, no steps can be observed for which the molecular C/A ratio in the solid phase is 2, 3, or 4.

Finally, in 1956, Lea [32] reported that the experiments by Brocard [7] had been repeated at the Building Research Station, and that the X-ray examination of the solids obtained failed to show other compounds besides the hydrated di- and tetracalcium aluminates.

Hypothesis of a Hydrated Carboaluminate

Facing these uncertain data, some authors preferred not to give an opinion. The question was thus unresolved until, in 1956, Schippa and Turriziani [49] observed that between 15 and 20 °C, in the system Al_2O_3–CaO–H_2O, there does not exist a hexagonal hydrated compound in which the C/A ratio is 3, whatever be the time allowed for equilibrium, or whatever the values of the C/A ratio in the initial solutions. The samples they prepared from supersaturated lime and alumina solutions, which, according to D'Ans and Eick [17] must contain hexagonal C_3AH_{12}, contained only C_2AH_8 and C_4AH_{13} as solid phases as demonstrated by the X-ray diagrams they obtained. Moreover, in the course of the hydration of C_3A with a saturated lime solution, the authors observed only C_4AH_{13} and $Ca(OH)_2$ (essential lines at respectively 8.41 and 4.92 A). The same results were obtained for preparations made from a fresh alumina gel and lime.

Schippa and Turriziani remark, on the other hand, that the spectra published by Bunn and Clark [6], and by Brocard [7] are practically identical with that of a carboaluminate formulated $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}$aq., whose diagram is given in table 3 (*d* in A).

TABLE 3. *X-ray diffraction pattern of carboaluminate and patterns formerly attributed to* C_3AH_{12} (d *in* A)

$C_3A{\cdot}CaCO_3{\cdot}H_n$	C_3AH_{12}	C_3AH_{12}
Schippa and Turriziani	Bunn and Clark	Brocard
7.74	7.70	7.65
3.79	3.77	3.77
2.89	2.85	2.86
2.55		
2.43		
2.366		
2.177		
2.118		
2.023		
1.955		

This carboaluminate, as well as the tricarboaluminate $C_3A{\cdot}3CaCO_3{\cdot}nH_2O$, had been already prepared by Jones [22], who reported the compound in a communication made in 1938, at the Stockholm Symposium. At the same time, Bessey [4] also made a private communication on the same subject.

It may be seen that the diagram obtained by Schippa and Turriziani shows an important line at 7.74 A, while the important lines given for C_3AH_{12} correspond generally, to lesser values (7.65 A, Brocard; 7.65 A, Govoroff; 7.70 A, Bunn and Clark.

Discussing the importance of this carboaluminate, Schippa, in another publication [50], insisted on the necessity of undertaking the study of the quaternary system Al_2O_3–CaO–CO_2–H_2O, and thus completing the study of the system Al_2O_3–CaO–H_2O.

Various investigators agreed with the conclusion of Schippa and Turriziani:

(1) Roberts [46], 1957, thinks that, the presence of CO_2 being unavoidable in the experiments and the carboaluminate being formed quite easily, it is probable that the compound first supposed to be C_3AH_{12} is nothing else than $C_3A{\cdot}CaCO_3{\cdot}H_n$.

(2) Carlson [15], 1958, having obtained in the course of his experiments hexagonal crystals whose composition was near enough C_3AH_{10}, hoped to verify that it was a hexagonal tricalcium aluminate, but, reading the work by Schippa and Turriziani published in the meanwhile, considered the question as settled.

(3) Buttler [11] on one hand, and Percival and Taylor [44] on the other, in their studies of the system Al_2O_3–CaO–H_2O at 5 and 21 °C, recognized the presence of $C_3A{\cdot}CaCO_3{\cdot}H_n$ in many preparations by the presence of the line at 7.6 A.

(4) On the other hand, Farran [19] in 1956, in his examination of the interfacial films between hardened high-alumina-cement pastes and aggregates on glass pans, attributed, as already mentioned, the presence of lines at 7.7 and 3.8 A to the existence of a solid solution of C_4AH_{13} and $C_3A{\cdot}CaCO_3{\cdot}H_n$. Farran determined also the refractive index of this carbonated compound as $n_\omega = 1.552$ and $n_\epsilon = 1.532$, those generally published as characteristic of C_3AH_{12} being $n_\omega = 1.550$ and $n_\epsilon = 1.530$.

In the actual state of our own results, the existence of C_3AH_{12} appears hypothetical. Working effectively, as far as possible, in absence of CO_2, we have been unable to prepare, as were Schippa and Turriziani [49], a compound of C/A ratio of 3. The X-ray diffraction spectrum of the product obtained shows the presence of lines indicating large interplanar spacings at 10.6 and 8.33 A which are those of C_2AH_7 and C_4AH_n. The X-ray pattern of the same product after submission to the action of CO_2 in moist atmosphere at about 20 °C indicates the disappearance of the line at 8.33 A and the appearance of a very strong line at 7.65 A, tending to prove that C_4AH_n has been transformed into monocarboaluminate with the C_2AH_8 remaining unaltered.

In any case, it must be noted that the authors who support the existence of C_3AH_{12}, do not mention the carbonate content of the compound studied. On the other hand, it is to be noted that according to a recent publication by Percival and Taylor [45] (see the following section) the line near 7.65 A could equally correspond to C_2AH_5, a partially dehydrated product of C_2AH_8.

Their comment cannot facilitate the resolution of this problem. In some cases, indeed, it is quite possible that the line at 7.65 A observed in the preparations may be a consequence of this partial dehydration, as seems to be the case, particularly, in our own experiments.

Dehydration of Aluminates

There is great variation in the number of molecules of water of crystallization attributed to the various hydrated aluminates as reported by different authors. It seems that, generally, at least a part of this water is bound in a rather loose manner and can be eliminated easily by raising the temperature only a few degrees, or by modifying the vapor pressure of the ambient atmosphere. It is normal that under these conditions disagreements between investigators should appear and that, in particular, the attribution of X-ray diagrams and of optical characteristics to definitely formulated hydrates should be difficult. A certain number of authors, whose works are summarized hereafter, have been preoccupied by these dehydration phenomena.

Hexagonal Tricalcium Aluminate

This compound, which is considered hypothetical by a number of investigators, has been the object of only a few publications during the last 10 yr.

Govoroff [24] thinks it is the stable compound up to 80 °C and that it represents, at this temperature, the product of the last stage of the dehydration of hexagonal aluminates. For samples heated between 20 and 80 °C, the essential line always observed in the X-ray pattern is situated, according to Govoroff, at 7.65 A.

The water content of hexagonal tricalcium aluminate is extremely variable, passing, according to the authors, through the values 2, 4, 6, 8, 9.5, 10.5, 12, or 14 (Assarsson [2]; Bessey [4]; Lefol [33]; Thorvaldson, Grace, and Vigfusson [54]).

Hexagonal Dicalcium Aluminate

The dehydration of hexagonal dicalcium aluminate has been studied by Roberts [46], Carlson [15], McMurdie [39], and Buttler [11] and has been recently reexamined by Percival and Taylor [45].

It seems that the water in the compound C_2AH_n presents a marked zeolitic character. McMurdie has shown that the loss of two moles of water takes place without important change in the crystal lattice, except perhaps a slight shortening of the c axis. In addition, Buttler noted that the dehydration curve for C_2AH_8 does not present steps, but only slight modifications of the slope of the curve at 50, 100, and 175 °C. On the other hand, it seems almost certain that C_2AH_8 exists in two polymorphic forms, α and β, whose essential lines are at 10.7 and 10.4 A (Roberts, Buttler).

Table 4 gives the characteristics defined by various workers, for various hydrates which were obtained by raising the temperature or by a change of the relative humidity of the atmosphere.

TABLE 4. *Characteristics of dicalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)	D	Refractive index
Salmoni [48], Carlson	11	10. 8–10. 9	------	------
Roberts, Buttler	8 (α)	10. 7	1. 95	1. 520–1. 505
Percival and Taylor.	8 (β)	10. 4	------	------
Roberts, Percival, and Taylor	7. 5	10. 6	1. 98	1. 520–1. 505
McMurdie	6	------	------	------
Roberts,	5	8. 7	2. 09	1. 534–1. 524
Percival, and, Taylor.	5 (little cryst.)	7. 6	------	------
Roberts, Percival, and Taylor	4	7. 4–7. 2	2. 27	1. 565–1. 559

Until the content of water of crystallization is reduced below 5 H_2O, the transformation is reversible, but the hydrate with 4 H_2O cannot rehydrate, whatever may be the hygrometric conditions.

Hexagonal Tetracalcium Aluminate

The dehydration of this compound has also been studied by Roberts [46], who attributes to the product a water content of 13 molecules. It seems probable, however, that in the presence of the solution the compound may be formulated C_4AH_{19}, the passage to 13 H_2O being easily and reversibly made by drying.

The compound with 13 H_2O can exist in two polymorphic forms α and β (D'Ans and Eick [17], Roberts). This hydrate can easily lose two molecules of water, by a transformation which also is reversible. A more pronounced loss of water probably induces a breaking of the crystal lattice, which can be seen in the aspect of the X-ray diagram.

The dehydration curve of C_4AH_{13} has been studied by Buttler [11]; contrary to that for C_2AH_8, it presents distinct steps at 50 and 108 °C. Between 160 and 400°, the curve is a continuous one until a content of 3.5 moles of water is reached.

Table 5 summarizes the results obtained by various investigators.

From the crystallographic point of view, the loss of 2 molecules H_2O, from 13 to 11, is recognizable by a slight shortening of the *c* axis, but up to this point, the unit cell may regain its previous dimensions by rehydration (Dent [18]). Between 150 and 300° C, on the contrary, one can observe a partial dehydroxylation, and the reversibility is surely no longer possible.

TABLE 5. *Characteristics of tetracalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)	D	Refractive index
Roberts	19	10.6	1.79	1.500-1.485
Roberts	13 (α)	8.2	--------	------------
D'Ans and Eick	13 (β)	7.9	2.02	1.536-1.519
Roberts	11	7.4	2.08	1.539-1.524
Roberts	7	7.4	2.28	1.555-1.544
Buttler	3.5	?	--------	------------

Monocalcium Aluminate

The formula CAH_{10} was proposed by Assarsson [3] as early as 1936. Like the previously mentioned aluminates, this compound may easily lose its water of crystallization by heating or by modification of the hygrometric conditions. It is probable that the formula CAH_{10} is only an approximate one, and both Longuet [37] and Carlson [15] have described a CAH_7 hydrate. The loss of water does not modify the crystalline structure since the differences which can be observed in the respective positions of the lines in the X-ray diagram, do not exceed 0.02 A.

Buttler [11], who determined the dehydration curve of this hydrate, notes that it does not present steps, but around 100 °C, for a composition CAH_4, the X-ray diagram is modified and the essential line at 14.6 A has disappeared. At the same temperature, Longuet observed a hydrate $CAH_{2.5}$ giving no X-ray diagram and beyond 880 °C, Schneider [51] found CA, whose presence indicated that the dehydration was complete. These results are summarized in table 6.

TABLE 6. *Characteristics of monocalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)
Brocard Carlson Midgley [36] Longuet	10	14.3–14.6
Longuet Carlson	7	13.6
Buttler	4	------------
Longuet	2.5	------------

Cubic Tricalcium Aluminate

Schneider [51] studied the dehydration of C_3AH_6 by differential thermal analysis and observed two endothermic peaks at 340 and 550 °C, corresponding to successive dehydrations that he has not identified. Beyond 550 °C, he identified the formation of the two crystalline phases $C_{12}A_7$ and CaO.

Monocarboaluminate

Turriziani and Schippa [56] have studied the behavior of $C_3A \cdot CaCO_3 \cdot H_n$ at various temperatures. It is not possible to consider this behavior as a true dehydration but rather as an ignition loss, CO_2 being eliminated with H_2O. The authors, therefore, proceeded by comparison with $CaCO_3$. Water is entirely eliminated at 600 °C; at this temperature, the quantity of CO_2 eliminated is 23.2 percent of the theoretical quantity, against 0.03 percent for $CaCO_3$. The original X-ray diagram of the carboaluminate persists up to 500 °C, proving that the unit cell is not modified up to this point.

The studies made in recent years show that water in the hydrated calcium aluminates is loosely bound to the remaining molecule. The removal of water molecules, when it is important enough, is accompanied by a modification of the dimensions of the unit cell. Consequently, to be satisfactorily significant, the X-ray diagrams should be accompanied by a verification of the water content of the aluminate examined. This verification is especially important as the partially dehydrated compounds may present lines very near the lines of other aluminates (see the section on "Hexagonal Tricalcium Aluminate—Carboaluminate"). Moreover, dehydration, in some cases, makes the X-ray diagram disappear: this "amorphization" is comparable with the phenomena described by Mlle. Couillaud [16], in her thesis in 1945, for which no valid explanation has been given until now.

One is tempted to think that, at least in certain cases, identification with the help of X-ray techniques is not enough. Perhaps it would be desirable to try the value of infrared spectrography in this particular domain as Lehmann and Dutz [34] have started to do.

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Discussion

M. H. Roberts

With regard to M. Lhopitallier's review of the equilibria in the $CaO–Al_2O_3–H_2O$ system, it may be noted that a detailed study of this system at 25 °C has recently been made by Jones and Roberts [1]. Some of the results and conclusions given in this paper and a reinterpretation of results previously obtained by other workers have already been discussed by Jones [2] in another paper in this Symposium. In addition, however, Jones and Roberts discussed briefly the problem of carbonation of solid phases, and confirmed Lhopitallier's conclusion that confusion has arisen between $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ and the alleged compound $C_3A{\cdot}12H_2O$. Carbonation, if it occurs to an appreciable extent, may have an important influence on any studies in the cement-water system, and the CO_2-containing aqueous systems therefore seem to warrant detailed investigation. In this connection, some limited tests have recently been done at the Building Research Station to examine the effect of the presence of carbonate on the equilibria in some CaO and Al_2O_3-containing aqueous systems at 25 °C. These involve shaking mixes of supersaturated monocalcium aluminate solution with lime to precipitate hydrated calcium aluminates, adding various amounts of $CaCO_3$, or Na_2CO_3, or each of these carbonates together with $CaSO_4{\cdot}2H_2O$, followed after further shaking by filtering, analyzing the filtrates, and examining the moist solid phases formed, by X-rays. Even with the relatively insoluble $CaCO_3$, it was found that complex carbonate compounds or solid solutions were usually formed, though after the shaking period (usually 7 days) a trace or a small amount of unreacted $CaCO_3$ was also present in most of the final solid phases.

With the supersaturated monocalcium aluminate solution without added lime, which precipitated mixtures of $C_2A{\cdot}8H_2O$ and hydrated alumina at 25 °C, in the presence of added $CaCO_3$ $\left(\text{initial } \frac{CaCO_3}{Al_2O_3}=0.66\right)$ no $C_2A{\cdot}8H_2O$ was formed. X-ray examination of the moist final solid phase showed only the presence of much $C_3A{\cdot}CaCO_3{\cdot}aq.$, some $A{\cdot}3H_2O$ and some unreacted $CaCO_3$. The final solution composition (0.193 g CaO per liter, 0.091 g Al_2O_3 per liter) was also markedly different from that observed in the absence of $CaCO_3$ (0.48 g CaO per liter, 0.24 g Al_2O_3 per liter). With additions of $CaCO_3$ $\left(\text{initial } \frac{CaCO_3}{Al_2O_3}=0.33 \text{ and } 0.66\right)$ to precipitated $C_2A{\cdot}8H_2O$ there was no marked change in solution composition but in addition to

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$C_2A{\cdot}8H_2O$ the final solid phase contained some $C_3A{\cdot}CaCO_3{\cdot}aq.$, a little unreacted $CaCO_3$, and with the larger addition of $CaCO_3$ some hydrated alumina as well. Additions of varying amounts of $CaCO_3\left(\text{initial }\frac{CaCO_3}{Al_2O_3}=0.33,\ 0.66,\ 1.0,\text{ and }1.2\right)$ to precipitated $C_4A{\cdot}19H_2O$ resulted in an apparent increase in the lime concentration of the solution, while the Al_2O_3 concentration decreased. At the same time the $C_3A{\cdot}CaCO_3{\cdot}aq.$ compound and what appears to be a $C_3A{\cdot}CaCO_3{\cdot}aq.$–$C_4A{\cdot}aq.$ solid solution phase (longest basal spacing varying between 8.3 A and 8.1 A) were formed, and except with the smallest addition of $CaCO_3$ the initially formed $C_4A{\cdot}19H_2O$ disappeared.

On adding similar amounts of Na_2CO_3 to precipitated $C_4A{\cdot}19H_2O$ almost all of the Al_2O_3 was removed from solution, and either the solid solution phase or a mixture of this with $C_3A{\cdot}CaCO_3{\cdot}aq.$ was formed. The amount of $C_3A{\cdot}CaCO_3{\cdot}aq.$ in the final solid phase increased with increasing additions of Na_2CO_3 until with an initial $\frac{Na_2CO_3}{Al_2O_3}$ molar ratio of about 1 almost pure $C_3A{\cdot}CaCO_3{\cdot}aq.$ was obtained. Larger additions of $Na_2CO_3\left(\text{initial }\frac{Na_2CO_3}{Al_2O_3}=1.9\text{ and }2.8\right)$ were also tried to see whether the carbonate analog of high sulfate sulfoaluminate, $C_3A{\cdot}3CaCO_3{\cdot}aq.$, could be formed, but only mixtures of $C_3A{\cdot}CaCO_3{\cdot}aq.$ and $CaCO_3$ were obtained.

With additions of $CaSO_4{\cdot}2H_2O$ together with $CaCO_3\left(\text{initial }\frac{CaSO_4}{Al_2O_3}=0.9,\text{ and }\frac{CaCO_3}{Al_2O_3}=0.8\right)$ to precipitated $C_4A{\cdot}19H_2O$, instead of obtaining $C_3A{\cdot}CaSO_4{\cdot}aq.$ alone, the presence of $CaCO_3$ resulted in the formation of a mixture of $C_3A{\cdot}3CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaCO_3{\cdot}aq.$, and a probable $C_3A{\cdot}CaCO_3{\cdot}aq.$—$C_4A{\cdot}aq.$ solid solution phase. A little unreacted $CaCO_3$ was also still present. With larger amounts of $CaSO_4{\cdot}2H_2O\left(\text{initial }\frac{CaSO_4}{Al_2O_3}=3\right)$ and with initial $\frac{CaCO_3}{Al_2O_3}$ ratios of 0.8 and 1.9, X-ray examination of the final solid phase showed only the presence of $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and calcite. There was no indication of the formation of $C_3A{\cdot}3CaCO_3{\cdot}aq.$ or a possible $C_3A{\cdot}3CaCO_3{\cdot}aq.$—$C_3A{\cdot}3CaSO_4{\cdot}aq.$ solid solution phase, the X-ray pattern observed for the high sulfate sulfoaluminate in these mixes containing carbonate being identical to that of the pure compound. Similar results to the above were also obtained with additions of mixtures of $CaSO_4{\cdot}2H_2O$ and Na_2CO_3.

From the above results, it is clear that the presence of calcium carbonate or alkali carbonate, or even exposure to atmospheric CO_2, may have a marked effect on the solution equilibria in the CaO–Al_2O_3–H_2O and related systems, and on the solid phases formed. Further work is required to establish the solution equilibria and solid phases formed in the presence of carbonate more precisely.

Paper VIII–S1. The Risk of Unsoundness Due to Periclase in High-Magnesia Blast-Furnace Slags*

N. Stutterheim

Synopsis

The production of slag as a waste product of blast-furnace operation is increasing, and interest in its utilization is growing. This is true also for high-magnesia slags.

It is evident from specifications for cement incorporating slag that there is a belief that magnesia unsoundness can occur with such slags, in a way analogous to the unsoundness which develops in portland cements with high magnesia content. However, the consensus of opinion among those who have experience with high-magnesia slags is that there are no grounds for this belief.

Experimental work done by the author has shown that cements made with granulated slags having from 13 to 21 percent of MgO yield sound concrete even after many years of moist storage. A study of the phase composition-liquidus temperature relationships was made, and it was found that those compositions in which periclase occurred either were near the periclase boundary, or their liquidus temperatures were high. Hence either they would not yield much periclase on cooling, or they would be unsuitable for blast-furnace operation because their effective viscosity, increased by periclase crystals in the slag, would be excessive. Work done by investigators on the optimum compositions for blast-furnace slags confirms this view.

It can therefore be concluded that the possibility of periclase formation in high-magnesia blast-furnace slags is remote, a conclusion which finds support also in the virtual absence of mention in the technical literature of periclase as a slag mineral.

Résumé

La production de laitier comme produit résiduel de l'opération des hauts-fourneaux augmente et avec elle s'accroît l'intérêt pour son utilisation. Ceci est vrai aussi pour les laitiers à forte teneur en magnésie.

Les stipulations pour le ciment incorporant le laitier indiquent clairement qu'il existe une croyance que l'inconstance de volume à cause de la magnésie peut se produire avec de tels laitiers, de façon analogue à l'inconstance qui se développe dans les ciments Portland à haute teneur en magnésie. Cependant, l'opinion est unanime parmi ceux qui ont fait des recherches avec les laitiers à forte teneur en magnésie que cette croyance n'est pas fondée.

Un travail de recherche effectué par l'auteur indique que les ciments faits de laitiers granulés contenant de 13 à 21% de MgO donnent un beton solide même après plusieurs années de conservation humide. Une étude des relations: composition de la phase—température liquidus fut faite et on trouva que les compositions dans lesquelles la périclase se produisait étaient soit celles proches de la limite de la périclase, soit celles dont les températures liquidus étaient hautes. De ce fait, ou elles ne produisaient pas beaucoup de périclase sur le refroidissement, ou elles ne convenaient pas à l'opération de haut-fourneau parce que leur viscosité effective, accrue par les cristaux de périclase dans le laitier, était excessive. Les travaux de recherche faits sur les conditions optimales pour les laitiers de haut fourneau confirment cette opinion.

Par conséquent on peut conclure que la possibilité de la formation de périclase dans les laitiers de haut fourneau à forte teneur en magnésie est peu probable, conclusion supportée aussi par le fait que dans la littérature technique il n'est virtuellement pas fait mention de la périclase en tant que minéral de laitier.

Zusammenfassung

Mehr und mehr Schlacke wird als Abfall in den Hochofenbetrieben hergestellt, daher ist man immer daran interessiert, wie man für eine solche Schlacke ein Awendungsgebiet finden kann. Das trifft auch für solche Schlacken zu, die viel Magnesia enthalten.

Wenn man sich die Normen durchliest, die die Zementindustrie für das Einverleiben der Schlacke in Zemente aufgestellt hat, bemerkt man sofort, daß die Industrie gegen einen hohen Magnesiagehalt ihre Bedenken hatte, welcher vermutlich von den schlechten Erfahrungen, die man mit magnesiareichen Portlandzementen gemacht hat, herrührt. Die Parteien, welche Schlacken, die magnesiareich waren, aufgearbeitet haben, weisen darauf hin, daß alle Furcht hier unbegründet ist.

Experimentalarbeiten des Vortragenden haben bewiesen, daß Zemente, die mit granulierten Schlacken mit 13–21% MgO-Gehalt hergestellt worden sind, einen guten Beton ergeben, der noch nach vielen Jahren Aufbewahrung in einer feuchten Umgebung zufriedenstellende Eigenschaften aufweist. Eine Untersuchung der Beziehungen zwischen Phasenzusammensetzung und Liquidustemperaturen zeigte, daß alle die Zusammensetzungen, in welchen Periklas auftritt, entweder sich in der Nähe der Periklasgrenze befinden, oder daß ihre Liquidustemperatur hoch ist. Das heißt, daß sie beim Abkühlen nicht viel Peri-

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klas hervorbringen, oder dass sie für das Arbeiten im Hochofen nicht benutzt werden können, da ihre Viskosität in der Gegenwart vieler Periklaskristalle in der Schlacke zu hoch liegen würde. Die Arbeiten, die über die beste Zusammensetzung der Hochofenschlacken veröffentlicht worden sind, bestätigen diese Ansicht.

Man kann daher schließen, daß eine Periklasbildung mit magnesiareichen Hochofenschlacken nicht zu befürchten ist, was auch dadurch bewiesen ist, daß Periklas fast nie in der Literatur als Schlackenmineral erwähnt worden ist.

Introduction

In his excellent review [1][1] of the state of knowledge concerning slag cements, as presented to the Third International Symposium on the Chemistry of Cements, Keil indicated that our knowledge of slag cements is not as far advanced as that of portland cements. Clinker is largely crystalline, so that its composition can be studied effectively by techniques such as those involving the microscope and X-ray and electron diffraction; on the other hand, the constitution of granulated slags as used for cement, being largely glassy, is more difficult to study. Moreover, portland cements have been known for a longer time and are applied in more ways than slag cements; also the tonnages employed far exceed those of the latter. It is not surprising, therefore, that more scientific endeavor has been devoted to the behavior of portland cement and more progress made in elucidating its constitution.

Blast-furnace slag is being produced in ever-increasing quantities, world production being roughly proportional to the output of steel. Having performed its metallurgical function, most slag has only nuisance value and is generally dumped. Because of the increasing value of industrial land required for dumping, the economic need for utilizing waste materials, and the ever-growing demand for mineral products, blast-furnace slag is being used increasingly for various purposes, particularly for cement manufacture.

Not all slags are considered suitable for the latter purpose. Several specifications for cements in which slag is incorporated place limitations on composition and, in particular, on the magnesia content of the slag. The limit for magnesia has been introduced to eliminate the risk of delayed unsoundness due to the presence of periclase in cement made from slag, using the experience with magnesia in portland cement as an analogy. For this reason, many cement technologists consider high-magnesia slags unsuitable for cement manufacture.

However, in many countries blast-furnace operators use magnesian limestone or dolomite as a blast-furnace flux, for technical or economic reasons. Interest in the possibility of utilizing the resultant high-magnesia slag for the manufacture of constructional cements has grown considerably in the last three decades.

General Methods of Using Slag for Cement Manufacture

There are two general ways in which a slag can be used for cement production:

1. As a raw material for the manufacture of portland cement clinker;
2. As a major ingredient of a slag cement for which the slag, in the rapidly chilled form, is finely ground and mixed with substances capable of releasing the latent hydraulicity of the slag.

High-magnesia slag cannot be employed in any quantity as a raw material for portland cement manufacture in view of the well-established risk of unsoundness with portland cements in which the magnesia content exceeds about 4 percent [2, 3]. This paper is concerned only with the second use of high-magnesia slag mentioned above.

Magnesia and Periclase in Cements

The only known form of free magnesia is periclase, an isotropic crystalline mineral whose hydration is associated with an increase in volume of the order of 110 percent of the original volume. The rate of hydration, unlike that of CaO, is slow; it depends on the temperature of periclase formation [4], on the periclase grain size [4, 5], and on external conditions; for instance, whereas CaO hydrates in the presence of both liquid and gaseous water, MgO appears to hydrate only in the presence of water in the liquid phase [4].

Free magnesia, i.e., periclase, is therefore responsible for magnesia unsoundness. If the magnesia is combined to form a compound, or if it is dissolved in a glass, it no longer expands on hydration. [3, 6]

High magnesia content per se in a slag, is therefore not an indication that the material is necessarily unsound, though it can be said, particularly in view of the large volume of the periclase primary phase field in the quaternary system $CaO{-}MgO{-}Al_2O_3{-}SiO_2$, that there is a strong prima facie case for caution.

A number of investigators who have studied the feasibility of using high-magnesia slags for cement manufacture, have expressed opinions on the question of soundness. In a study of the strengths of slag-portland cement mixtures including, inter alia, some high-magnesia slags (range 7.2 to 18.5 percent of MgO), Grün [7] observed that there was no evidence of unsoundness up to 2 yr, and concluded that the MgO in slag is bound differently from that in portland cement clinker. Nurse and Midgley [8] examined the minerals present in slags of a wide range of compositions, including high-magnesia slags, but found no periclase.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Stutterheim and Nurse [9] found no unsoundness in portland blast-furnace cement concretes made with high-magnesia slags (15 to 18 percent of MgO) even after 3 yr moist storage; autoclave expansions of the cements ranged from 0.05 to 0.22 percent.

Schumann [10] reviews the question of limitations placed by various countries on the permissible MgO content of slags intended for cement manufacture, and concludes that there is experimental evidence and a considerable weight of opinion in favor of allowing fairly high contents, much higher than were laid down in the United States of America. Appiano [11] presents a similar review of evidence and draws attention to the undue restrictiveness in this respect of the present specification for slags in Italy. Cirilli and Brisi [12] describe a particular case of a slag with an MgO content of 32 percent which proved completely sound.

Hence, although these authors do not present many systematic experimental data, there is a consensus of opinion among those with experience of this type of material that high-magnesia slags are sound.

In 1947 the author started an investigation initially in collaboration with R. W. Nurse of the Building Research Station, England, and continued later at the South African Council for Scientific and Industrial Research, Pretoria, on the question of soundness of high-magnesia blast-furnace slags. This investigation involved a study on the system gehlenite-spinel [13], as well as an investigation of the performance of high-magnesia slags from iron works in the northeast of England [9], followed by an exploration of the region of compositions of slags as produced at blast-furnaces operated with dolomite fluxes in South Africa [14]. In the latter work an attempt was made to allow for the presence also of oxides other than CaO,MgO, SiO_2, and Al_2O_3 by using slag as parent material and modifying its composition as desired by fusion with known amounts of the required oxides or carbonates. Some of the results of the primary-phase and liquidus-temperature determinations are presented in table 1, the compositions being recorded as though the specimens were four-component mixtures. For the sake of brevity only some of the results, listed in increasing order of MgO content, selected from a series of 109 quench determinations and representative of the range of MgO contents examined, are given.

TABLE 1.—*Primary phases and liquidus temperatures for synthetic slags of high-magnesia content*

Quench specimen No.	Composition (calculated four-component)				Primary phase	Liquidus temperature
	SiO_2	Al_2O_3	CaO	MgO		
	%	%	%	%		° C
89	35.0	5.0	44.0	16.0	C_2S	1,650
80	42.0	5.0	37.0	16.0	Melilite	1,415
104	33.0	9.5	41.5	16.0	Merwinite	1,480
85	28.0	14.6	41.4	16.0	Periclase	1,490
81	28.0	24.1	31.9	16.0	Spinel	1,560
94	39.1	5.0	37.4	18.5	Periclase	1,500
13	39.6	12.9	28.9	18.6	Spinel	1,375
12	35.2	11.5	33.4	19.9	Spinel	1,380
79	37.4	5.0	36.8	20.8	Monticellite	1,410
41	35.9	7.5	34.7	21.9	Periclase	1,565
5	39.1	10.4	28.6	21.9	Forsterite	1,390
3	37.2	12.6	28.3	21.9	Spinel	1,390
31	32.5	14.0	31.5	22.0	Spinel	1,400
53	28.0	21.1	26.5	24.4	Spinel	1,590
87	36.8	8.0	29.6	25.6	Periclase	1,450
97	34.4	12.6	26.7	26.3	Spinel	1,470
48	31.1	15.5	26.8	26.6	Spinel	1,505
61	28.0	18.8	26.0	27.2	Periclase	1,570
52	38.4	5.0	29.1	27.5	Periclase	1,650
45	39.6	7.2	25.3	27.9	Forsterite	1,500
46	35.9	10.0	25.2	28.9	Forsterite-Periclase	1,475
38	34.4	12.8	23.9	28.9	Spinel	1,480
22	31.1	13.9	25.8	29.2	Periclase	1,600
62	28.0	18.7	23.3	30.0	Periclase	1,610
54	30.6	18.8	20.0	30.6	Spinel	1,595
63	39.9	5.0	23.9	31.2	Periclase	1,650
39	40.0	6.8	21.7	31.5	Forsterite	1,600
19	34.4	10.9	23.0	31.7	Periclase	1,540
18	35.8	12.5	19.6	32.1	Forsterite	1,560
47	28.6	18.9	20.0	32.5	Periclase-Spinel	1,610
59	39.7	6.8	20.0	33.5	Forsterite	1,650
64	36.6	9.9	20.0	33.5	Forsterite	1,550
70	35.6	10.9	20.0	33.5	Periclase	1,540

Those specimens having periclase as primary phase mostly have compositions which lie near the periclase phase boundary. Where this is not the case the liquidus temperatures are relatively high, and slags having such compositions would therefore not properly perform their metallurgical functions in a blast furnace, since their effective viscosities at normal furnace-operating temperatures would be too high. Even with slags having compositions just inside the boundary of the periclase phase field, operation could be difficult because small variations in composition could lead to relatively large variations in effective viscosity, which would interfere with furnace control. For this reason the composition region bordering on the periclase phase field would be avoided by blast-furnace operators.

There is a possibility that an occasional tapping of slag has a composition within the primary phase field of periclase, though it could never be far in, for reasons already mentioned. On cooling under conditions of equilibrium, therefore, this mineral will make its appearance, with the result that the point representing the composition of the residual liquid will move away from the MgO apex along a line connecting that apex to the point representing the gross composition of the slag. Since the periclase boundary is near, the amount of periclase which would crystallize out would be small. The greatest likelihood for trespass into the periclase region is where liquidus temperatures are lowest, i.e., adjacent to the primary phase fields of merwinite, monticellite, and spinel. These are so situated that during crystallization the composition of the residual liquid moves away from the periclase field. Consequently, the amount of periclase that would crystallize out even from such an improbable slag would, at worst, be small.

It is interesting to examine the results of other investigators who have studied the quaternary system CaO–SiO_2–Al_2O_3–MgO to determine optimum slag compositions for blast-furnace operation. In this respect the work of Osborne, De Vries, Gee, and Kraner [15] is particularly illuminating. They have the following to say about optimum blast-furnace slag compositions:

"For a blast-furnace to operate smoothly and with maximum efficiency, the slag should have the following characteristics:

"1. It should be a homogeneous liquid, that is, without notable variations in the properties of the liquid and without crystalline phases present.

"2. Its composition should be such that a wide latitude of variation in composition is possible without a troublesome slag developing. Under the best conditions of operation, raw materials vary sufficiently to cause significant variations in slag composition. The slag should tolerate such inevitable variations in composition without notable changes in its properties and performance.

"3. It should have a high potentiality for retaining sulfur.

"4. It should have a low viscosity at the temperatures prevailing in the furnace in order to melt down and move through and out of the furnace quickly and smoothly".

From these remarks it can be concluded that if the liquidus temperature of a slag is relatively high the slag will tend to be troublesome in the furnace, because its effective viscosity will increase markedly below this temperature. Moreover, in a region where the liquidus-temperature contours are steep, small changes in composition can lead to large variations in viscosity. It is therefore advisable to avoid operation near regions where this is the case, e.g., within the periclase and C_2S primary phase fields.

Hence, although there may be no concern on the part of blast-furnace operators about the nature of the particular primary phase which their slags would yield on cooling, there is much concern about the viscosity of the slag in the furnace. It is undoubtedly for this reason, that periclase is a rare, if not unknown, slag mineral.

It appears, therefore, that the composition-liquidus temperature relationships dictate the practical range of slag compositions and that, in a sense quite fortuitously, slags in the periclase primary phase region would have such variable properties and therefore such unpredictable performance characteristics that operators carefully avoid such compositions. Even if an occasional slag had a constitution falling within this region, which is possible though improbable, the amounts of periclase would at most be small, because the locus of points representing the composition of the residual liquid, after periclase starts crystallizing out, will move in the direction of the periclase boundary, which could never be far removed, because of the steep liquidus temperature contours of this primary phase region.

From the results of Osborn, De Vries, Gee, and Kraner it can also be deduced that if the composition of a slag falls just outside the periclase boundary, e.g., in the primary phase fields of merwinite, spinel, monticellite, or forsterite, the compositions of the liquid phase, as cooling occurs from the liquidus temperature, will follow paths which generally do not intersect the periclase boundary; for such slags no periclase can form.

The possibility of a slag falling within the primary phase field of C_2S is remote because, as in the case of the periclase primary field, here also the liquidus-temperature contours are very steep, and consequently such a slag would be troublesome in the furnace. However, there is a possibility that on occasion the composition of a slag might trespass into this field, although obviously only the low-temperature edge comes into consideration, i.e., the region below the 1,500 °C line. On cooling to below its liquidus temperature, the locus of points representing the composition of the residual liquid would move away from the point representing C_2S, until it reached the common boundary between the primary phase field of C_2S and merwinite; hence no periclase would form.

The various possibilities discussed in the previous paragraphs can be seen clearly from figure 1. This is part of the 10-percent Al_2O_3 plane of the quaternary system CaO–MgO–Al_2O_3–SiO_2 [15] with composition points representing various relevant minerals shown projected on it. The liquidus-temperature isothermals are shown, to indicate what composition fields come into consideration for slags free of crystalline phase while in the furnace. According to the authors quoted above, the components other than the four major oxides, normally found in blast-furnace slags to the extent of about 5 percent, tend to depress the liquidus temperature by about 100 °C below that corresponding to the relevant figure for pure quaternary mixtures. Since blast-furnace slags must be completely liquid at temperatures of the order of 1,400 °C or lower, the 1,500 °C liquidus-temperature contour in figure 1 is virtually a boundary in the sense that slags of compositions below it will be troublesome in the furnace. This contour has been drawn more boldly in the figure.

It is immediately apparent that very limited scope exists for operating blast furnaces with slags from which periclase could crystallize. Although only the 10-percent Al_2O_3 diagram is shown, examination of other sections through the composition tetrahedron lead to the same conclusion.

The considerations given above undoubtedly explain why the literature is virtually free of any reference to positive identification of periclase in blast-furnace slags. The author has found indirect evidence also, in that several hundred A.S.T.M. autoclave soundness tests have been carried out on cements in which high-magnesia slags were a major ingredient, without any expansion values in excess of 0.3 percent having been found. The slags concerned ranged in magnesia content from 13 to 20 percent.

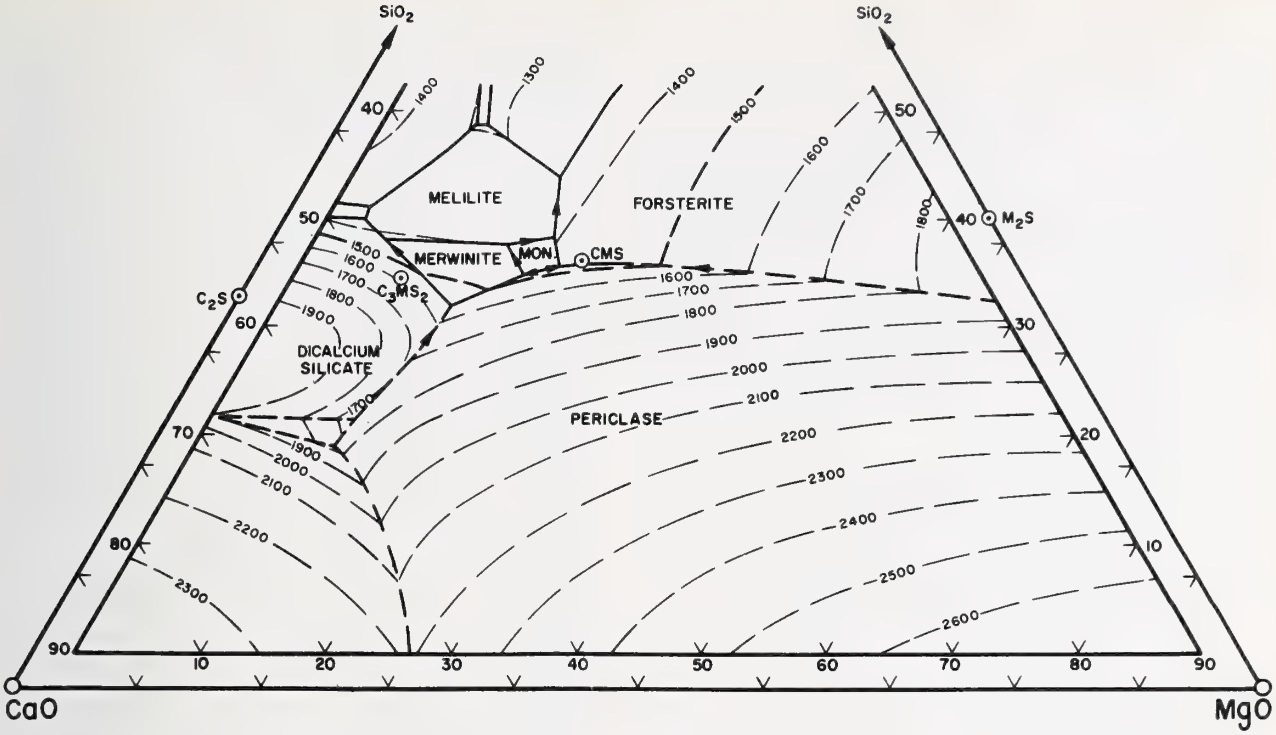

FIGURE 1. *Phase diagram for the quaternary system* CaO—Al_2O_3—SiO_2—MgO *at the 10-percent level.*

Temperature contours (°C) and other relevant data are superimposed.

Conclusion

It can be said that the possibility of periclase formation, and therefore of unsoundness due to this mineral in high-magnesia blast-furnace slags is remote.

Since, however, it cannot be said to be impossible, for reasons which must be clear from the discussion above, and since, furthermore, the use of a slag with several percent of magnesia could lead to disruption of a product made from it, care is required to insure that such material will never be used for cement manufacture. The granulation process, which is an essential one in the preparation of slag for cement manufacture, is, of course, aimed at insuring that the material is present in the glassy state. However, in practice this objective is never fully achieved, either because at the moment of granulation the slag is already below its liquidus temperature, or because the chilling process is not sufficiently rapid to prevent some crystallization.

There is, however, a very useful, practical, test in the form of the autoclave test, already referred to above, which allows one to distinguish between sound and unsound material. This test, which was specifically designed to establish whether periclase is present in portland cements, can be applied equally well to blast-furnace slags. By its adoption as a routine test procedure on all batches of granulates intended for cement manufacture, a relatively inexpensive means of insuring the use of sound material is provided.

In South Africa, portland blast-furnace slag cements have been used experimentally since 1948 in the laboratory, and since 1953 in pilot-stage field trials. Examination of the concrete made with this cement, under a wide variety of circumstances, has shown no evidence of unsoundness or poor durability. These experiments and trials have also proved that high-magnesia slags can have satisfactory cementitious properties, as already described elsewhere [16]. It is for these reasons that it became possible to produce cements having high-magnesia slag granulate as a major ingredient, on a commercial basis in South Africa. This is now a growing industry, which during the current year had a production of the order of 300,000 tons.

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Discussion

Levi S. Brown

Essentially this paper considers the effects of two pairs of extremes. One pair looks upon blast-furnace slag as either completely crystalline or all glass (water-granulated). The other pair considers the slag used as raw material in the manufacture of cement or as a finished material to be interground with cement clinker in preparation of slag cement.

As a raw component in the manufacture of cement, the crystalline or glassy state is of no moment nor is the chemical composition critical. The only requirement is that the chemical composition be known and that the proportion of the slag never be greater than that yielding maximum permissible chemical magnesia in the eventual portland cement. In view of these fixed limitations, the paper has no further concern with such use.

As an interground component of slag cement, however, the slag preserves its identity, and it is imperative to be properly advised as to occurrence of free magnesia in the slag. The paper devotes much attention to phase relations of systems appropriate to blast-furnace operation. It is shown that chemical magnesia may be high without occurrence or likelihood of occurrence of free magnesia. Such consideration assumes per se a complete crystallinity, whereby the magnesia content is largely tied up in minerals such as melilites, ferro-magnesians, or other magnesian silicates, which are stable and do not have the potentially damaging properties of periclase.

But, as noted in the paper, it is essential that granulated slag be used for slag cement manufacture, for the advantage of hydraulicity of the glassy state. Properties of the glass may be very different from those of the same composition completely crystalline. There may be no periclase perceivable as a unique phase. Yet the disorder of the glassy state implies that the magnesia is free and unbonded. May it not be regarded correctly as a distribution of periclase in units of molecular dimension?

This thought has rested with the writer since adoption in 1937 of the autoclave test for delayed unsoundness of portland cement. The notable reduction of autoclave expansion effected by quick cooling of clinker was well recognized. It was considered, by way of explanation, that magnesia as periclase was taken out of circulation by solution in the glass. But may not that be only a dispersion of molecular units? And may not a single molecule, unattached, have the same properties as a group of free molecules?

Introduction of these comments is made at this time to report an observation some time ago of an occurrence of slag disintegration that seemed to answer these questions. This was a blast-furnace slag with about 17 percent chemically determined magnesia. It had been effectively quenched, so that physically it was essentially a single phase, all glass, without perceivable periclase. The glass was minutely cracked. The fractures were lined with a uniform development of secondary brucite, indentified by unique optical properties of refractive index and birefringence. It was quite evident, further, that this secondary development was instrumental in the mechanics of disintegration of the slag.

It is indicated in this observation that a glassy slag high in magnesia may react and may function in a manner essentially similar to periclase. The paper suggests that the autoclave test, though specifically designed to establish whether periclase is present in portland cements, can be applied equally well to blast-furnace slags, to distinguish between sound and unsound material. Considering the above observation, the suggestion appears to be well taken, even though a comprehensive review of experience and experiment with blast-furnace slags and slag compositions shows performance to have been very generally good.

Closure

N. Stutterheim

Dr. Brown raises an interesting point, viz., whether the magnesia dissolved in a glass is not still capable of hydrating to form brucite and in the process to expand, so leading to unsoundness. He submits that the magnesia in a glass could well be present as unattached molecules and hence free to behave like crystalline periclase.

To clinch the point, he describes a case of a glass containing about 17 percent MgO which was microfractured, and secondary material in the cracks was identified as brucite.

If this were so then presumably all the oxides present in a glass would also behave as they would in the crystalline state. In particular, CaO in a glass would behave like free lime and in addition to brucite, hydrated lime should have been present in the microcracks and would have been a co-contributor to the observed unsoundness. Hence not only high-magnesia glasses but all high-lime glasses would be unsound. Is there any evidence for this?

The fractures in the high-magnesia slag particles, to which Dr. Brown refers, could perhaps have been due to stress-relief or to devitrification, in which cases brucite could still have developed subsequently. One would, however, expect other hydrates to be present too.

That magnesia present in a glassy slag could hydrate to form brucite is quite likely; but this does not necessarily mean that the reaction will be accompanied by unsoundness. Very finely divided periclase such as that formed when dolomite is burnt at temperatures below 900 °C exhibits no unsoundness upon hydration, even in the autoclave test [1]. The identification of periclase or of brucite must therefore not in itself be associated with unsoundness.

For magnesia unsoundness to occur, a prerequisite appears to be that the periclase is present in relatively large particles. The gross expansion in unsound paste, mortar or concrete is not equivalent to the volume increase associated with the $MgO \rightarrow Mg(OH)_2$ transformation, but is much greater, being due to opening up of cracks in a rigid material by the swelling particles. Hence a small number of large periclase particles will in general have a much more pronounced effect than an equal weight of smaller more numerous particles.

In South Africa more than a million tons of cement containing granulated high-magnesia slag as a constituent has been used under a wide range of conditions [2] and some of the concrete is now over 10 yr old. No evidence of periclase unsoundness has been observed in any of these applications, neither has any expansion beyond the acceptable limit been observed in the autoclave tests. In fact, as mentioned by Sandler during discussion at the Symposium sessions in Washington, any autoclave expansion in portland cement clinker, whether due to free lime or to free magnesia, is suppressed if slag (whether high-magnesia or not) is added as an admixture.

While therefore ready to agree with Dr. Brown that one cannot be dogmatic on this matter, the author submits that the evidence supports the view that high-magnesia blast-furnace slags do not lead to unsoundness in cements of which they form a constituent.

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Paper VIII–S2. Special Masonry Cement Having a High Slag Content*

S. Nagai

Synopsis

As the waste product of blast-furnace iron-making operation, water-granulated slag is being increasingly utilized in portland blast-furnace cement (in Japan about 1,500,000 to 2,000,000 tons per year in 1959 to 1960). This use of slag as an admixture to portland cement has gradually developed in the past 50 yr, but the use as slag-lime cement or masonry mortar cement is not well developed, owing to its slow and low hydration property. However, the special use of cement as masonry mortar for high concrete buildings and fireproof mortar plastering of wood buildings is a most urgent problem in Japan.

For this reason, the author during these years has studied high-slag-content lime cement for masonry mortar use, by the addition of accelerating agents for the latent hydraulic property of water-granulated slag. Admixtures of natural or industrial waste siliceous matter as pozzolanic materials, or fine granular fused matter such as fly ash, were used for the purpose of accelerating the development of strength and diminishing efflorescence, or decreasing the water-cement ratio, or increasing the plastering power of cement mortar.

From these many experimental results, the present author proposed the limiting values of various physical properties in the Japanese Industrial Standard Specification for masonry cement, which is expected to be enacted in the near future, by comparing them with those values in the Japanese Industrial Standard Specifications of portland cement (JIS R 5210), portland blast-furnace cement (JIS R 5211), and portland silica cement (JIS R 5211) which have been in force for many years.

Résumé

Le produit résiduel dans l'opération de la fabrication du fer dans les hauts fourneaux, le laitier granulé est utilisé de plus en plus dans le ciment portland au laitier de haut fourneau (au Japon 1,500,000 à 2,000,000 tonnes environ par an en 1959–1960). Cette utilisation du laitier en tant qu'addition au ciment portland s'est graduellement développée au cours des 50 dernières années, mais son utilisation comme ciment de laitier à la chaux ou ciment à maçonner n'est pas très développée, à cause de sa propriété d'hydratation lente et basse. Pourtant l'utilisation spéciale du ciment comme mortier de maçonnerie pour les constructions élevées en béton et le crépissage au mortier réfractaire des constructions en bois est l'un des problèmes les plus urgents au Japon.

Pour cette raison l'auteur au cours de ces dernières années a étudié le ciment de chaux à forte teneur en laitier pour l'usage du mortier de maçonnerie, en ajoutant des agents accélérateurs pour la propriété hydraulique latente du laitier granulé. Les additions de produits siliceux naturels ou de déchets industriels comme les matériaux pouzzolaniques, ou de fines matières granuleuses fondues telles que la cendre volante furent utilisées dans le but d'accélérer le développement de la résistance et de diminuer l'efflorescence ou de décroître le rapport eau-ciment ou d'accroître la puissance de crépissage du mortier de ciment.

A partir de nombreux résultats expérimentaux, l'auteur a proposé les valeurs limitatives des propriétés physiques variées dans les Normes de L'Industrie Japonaise pour le ciment à maçonner, lesquelles sont en cours d'être établies, de la même manière que les valeurs dans les Normes de L'Industrie Japonaise du ciment portland (JIS R 5210), le ciment portland au laitier de haut fourneau (JIS R 5211), et le ciment portland de silice (JIS R 5211), qui sont en usage depuis de nombreuses années.

Zusammenfassung

Als Abfallprodukt des Eisenhochofenprozesses wird wassergranulierte Schlacke mehr und mehr in Portlandhochofenzementen angewandt (in Japan hat man 1,500,000 bis 2,000,000 Tonnen im Jahr vom 1959 bis 1960 benutzt). Über einen Zeitraum von 50 Jahren hat man mehr und mehr gelernt, solche Schlacke dem Portlandzement zuzufügen, aber für Schlackenkalkzemente oder Maurerzementmörtel hat man nicht so gerne solche Schlacken beigegeben, weil sie so langsam hydratisieren. Nun ist gerade in Japan die Anwendung der Zemente als Mauermörtel für hohe Betonbauten und als feuerbeständige Mörtelbekleidung in Holzbauten von großer Wichtigkeit.

Aus diesen Gründen hat der Vortragende seit einigen Jahren Kalkzemente, die einen hohen Schlackengehalt haben, in ihrer Anwendung als Mörtel für Mauerwerk studiert; er hat Beschleuniger hinzugefügt, damit die latenten hydraulischen Eigenschaften der wassergranulierten Schlacken schneller zur Wirkung kommen. Beimischungen natürlicher oder künstlicher, kieselsäureenthaltenden Abfallprodukte, wie Pozzolane, oder eines feinkörnigen, geschmolzenen Materials, wie Flugasche, wurden benutzt, mit dem Gedanken, dadurch eine schnellere Entwicklung der Festigkeit, eine Herabsetzung der Ausblühungen, eine Verkleinerung des Wasser-Zementverhältnisses oder eine Erhöhung der Bewurfskraft der Zementmörtel hervorzubringen.

Auf der Grundlage seiner Versuchsergebnisse schlägt der Vortragende vor, Grenzwerte für die verschiedenen physikalischen Werte in die japanischen Industrienormen für Mauer-

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Faculty of Engineering, National University, Yokohama, Japan.

zemente einzuverleiben, und das soll schon ziemlich bald geschehen. Diese Normen werden mit den japanischen Normen für Portlandzemente (JIS R 5210), Portlandhochofenschlackenzemente (JIS R 5211) und Portlandquarzzement (JIS R 5211) in Einklang stehen. Diese anderen Normen werden schon seit vielen Jahren benutzt.

Introduction

Incombustible and fireproof buildings are now extremely important in Japan, owing to the existence of large numbers of wooden buildings. For this purpose, the walls and ceilings must be plastered, and also building brick, tile, concrete block, and artificial or natural stone must be cemented firmly by cement-sand mortar from so-called masonry cement. The ordinary cement mortar is made from common portland cement, various mixed portland cements such as portland blast-furnace cement, portland-pozzolan cement, portland fly-ash cement, etc., which are all covered by the Japanese Industrial Standard Specifications. But for the above-mentioned masonry-cement-mortar use, it is most important that the masonry cement must be cheaper than the cement for ordinary constructional or concrete use, and also must have many other useful properties, such as a somewhat slower set, strong cementing power, less expansivity, less shrinkage, less cracking tendency, less efflorescence, etc.

In Japan it is said that about 130 million square meters of wall and ceiling will be plastered with cement mortar in 1 yr, and about 800,000–900,000 tons of cement will be needed for this purpose. Again a nearly equal amount of masonry cement will also be used for mortar for common brick, tile, concrete block, natural or artificial stone, etc.

Principle of Study

The amount of cement for these two uses will be about 1.5–2 million tons, which is about 10–12 percent of all cement or about 25 percent of cement for all building (architectural) use. For these purposes, the present author has already for about 30–35 yr studied and reported [2] on various kinds of cement, as medium-strength cement, special mortaring cement, miscellaneous-use cement, various mixed or blended cements, as slag-lime or lime-slag blended, pozzolan-lime or lime-pozzolan cement, etc.

In these studies water-granulated blast-furnace slag was mainly used for the principal raw material for making the masonry cement. This point of view is derived from the following idea: In Japan about 9–10 million tons of pig iron is now manufactured in 1 yr, so that about one-half as much, or 4–5 million tons, of slag is obtained as byproduct. But only about 10–15 percent of the slag is water granulated and used for portland blast-furnace cement, slag-lime brick, and artificial stone or block, etc., a nearly equal part is used for ballast as gravel for road or railroad, and the other large part of the slag has now no use and is thrown into the sea, for reclaiming work at the seaside, etc.

This water-granulated or quenched slag has a latent hydraulic property, but the setting and hardening properties are very slow and weak, without other effective additional substances for accelerating this latent hydraulic property. For this stimulation, acceleration, or promotion of latent hydraulicity of water-granulated slag, slaked lime is commonly added, but its accelerating power is not great and sometimes a siliceous admixture must be added, when excess slaked lime or free calcium hydroxide is left over. The author has studied the stronger special accelerating agents such as chemical reagents in water solution or mortaring dilute solutions, or in the state of very fine powder added to the cement samples, in both cases the quantity being very small (about 2–3 percent).

Cement Samples

In the present studies, water-granulated slag was obtained from different iron works, analyzed chemically, examined as to its suitability for use as the main raw material of the masonry cement (about 50–70 parts), and then powdered to a fineness of about 1.4 percent residue on the 4,900-mesh sieve (170 meshes/in. or 0.088 mm or 88 μ).

The second raw material, the lime-bearing component, as accelerating or hardening admixture to the slag powder above prepared, is slaked lime from a quicklime slaking plant, or from a carbide-acetylene plant. This slaked lime has proved to be suitable as the second component of the present masonry cement. It contains 69–72 percent of CaO, about 23–27 percent loss on ignition (inclusive of combined water, CO_2, etc.), a very small amount (less than 1 percent) of SiO_2, Al_2O_3, Fe_2O_3, MgO, etc., which are nearly negligibly small impurities in the preparation of the masonry cement. Its fineness is very high, it being the chemically hydrated product of slaking quicklime or of decomposing calcium carbide with water. As the third raw material or admixture, various siliceous materials of natural origin, or waste byproducts from various chemical or metallurgical industries were used. One kind of siliceous admixture was fly ash from fine-coal-firing boilers of hydroelectric power plants, and the others were the siliceous residual matter or byproduct containing a large content of silica (about 90–92 percent), obtained from acidic hot springs, or from a pressure steam sulfur refinery plant. These three kinds of siliceous raw materials were analyzed and powdered to about 1–3 percent residue on the 4,900-mesh sieve. These siliceous admixtures were used in the mixing proportion of about 10–30 parts in the masonry cement samples.

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[2] J. Japan. Ceramic Assoc. **41,** p. 399 (1933), **49**. p. 674 and 745 (1941), **51,** p. 488 (1942), **62,** p. 403 (1954); J. Soc. Ind. Chem., Japan **38,** p. 431 and 1137 (1935), **39**. p. 304 (1936); Gypsum & Lime, No. **32,** p. 1553 (1958), No. **35,** p. 5 (1958), No. **37,** p. 18 (1958), No. **40,** p. 12, No. **41,** p. 19 (1959).

These three kinds of components, slag, lime-bearing, and siliceous admixture, as above mentioned, for the masonry cement manufacturing, were intimately mixed and ground to fine powder in the following ratios: slag: 50–70 parts; slaked lime: 10–30 parts; siliceous matter: 10–30 parts. Many series of masonry cement samples were prepared by the same procedure. One masonry cement sample was obtained from the market and included for comparison.

Testing Methods

These prepared samples of masonry cements were tested for their various physical properties and chemical compositions. The analyses for chemical composition, and the testing of setting time of neat cement paste and bending and compressive strengths of 1:2 cement-sand mortar in prismatic (4 x 4 x 16 cm) test pieces were carried out by the testing methods in the Japanese Industrial Standard Specifications for cement (JIS R 5201 and 5202). The mixing water for neat cement paste for the setting-time test and for 1:2 cement-sand mortar-strength tests (bending and compressive strengths) was replaced by various dilute solutions (about 1–3 percent) of NaOH, Na_2CO_3, Na_2SiO_3, Na_2SO_4, etc., and the effects of these salts on the setting time and strength were compared with those obtained with water. The solutions proved clearly to be very effective in quickening the slow setting time and in increasing greatly the low strengths of these masonry cements, especially at earlier curing ages (3–7 days).

These inorganic salts were added in general in dilute solution, instead of mixing water, but in several cases were tested by adding very fine powder of Na_2CO_3 or Na_2SO_4 to the cement samples and mixing with water. The dilute solutions (about 1–3 percent) of these inorganic chemical salts were used in amounts of about 60–65 parts to 100 parts of masonry cement for mixing (or a water cement ratio of 0.60–0.65). Thus the amount of these salts in this volume of solution was only about 0.5–1.5 percent of the weight of the cement, which is a very small proportion of the cement mortar and less than the amount of gypsum in portland cement and various mixed cements such as portland blast-furnance cement, portland-pozzolan cement, portland fly-ash cement, etc.

The hardening of these masonry cements is very slow, in the case of mixing with water, but it can be accelerated by mixing with dilute solutions of NaOH, Na_2SiO_3, Na_2SO_4, etc., and the hardened strengths are high, quite enough for masonry-mortar use, even at short curing ages (less than 3–7 days).

Experimental Results

Many series of special cement samples for masonry-mortar use were prepared by the methods described above, using mainly granulated blast-furnace slag as the principal component, and siliceous and calcareous admixtures were mixed in reasonable amounts to accelerate the latent hydraulic property of the granulated slag. For mixing these three components, granulated slag powder, siliceous admixture, and slaked lime with fresh water, the common testing method was first carried out. Then the dilute solution of inorganic salt (NaOH, Na_2SO_4, etc.) was used for mixing, resulting in remarkably superior strengths. Especially, cement dust from the electric dust catcher, containing Na_2O, K_2O, and CaO, as Na_2SO_4, K_2SO_4, and $CaSO_4$, with some amount of free lime, gave superior results in various physical and chemical tests. In the following sections, test results of various series of prepared cement samples are reported and compared with those of common tests using fresh water.

First Series of Experiments

Two kinds of granulated slag powder, one kind of slaked lime, and fly ash from a powdered-coal-firing electric-power plant, were analyzed and the results are tabulated in table 1.

Two kinds of masonry cement samples were prepared by mixing these three raw materials, finely ground in the various ratios shown in table 2, and the results of tests on their sieve fineness and chemical composition are shown also in table 2.

These cement samples were tested for their setting and hardening properties, by the Japanese Industrial Standard Specifications method for portland cement and various mixed portland cements. The bending and compressive strengths were tested by 1:2 cement-sand plastic mortar. These results were shown in table 3.

From these results, the special masonry cements prepared by the author by using a large amount of granulated slag with siliceous admixture and

TABLE 1. *Chemical compositions of raw materials*

(Percent)

	Loss on ignition	Insol. Res	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Sulfide sulfur
Slag (1)	0.72	0.80	34.31	16.54	1.43	37.35	5.54	0.03	1.08
Slag (2)	.43	.28	33.75	18.00	1.03	39.14	5.76	.12	1.05
Slaked lime (1)	23.85	.23	.17	.18	.15	73.29	1.46	------	------
Fly ash (1)	.34	3.53	60.73	22.15	8.63	3.63	1.04	------	------

slaked lime, specially accelerated by dilute alkaline water, hardened quickly with remarkably high strengths at 7 and 28 days in air and even higher strengths when cured in water. The dilute caustic soda (NaOH) solution was better than the carbonate (Na_2CO_3) solution, owing to the reaction of Na_2CO_3 with slaked lime ($Ca(OH)_2$) to give $CaCO_3$. The dilute NaOH solution gave strengths about 2–3 times greater than those with fresh water. This increase is due to the remarkably beneficial effect of dilute alkaline solutions in accelerating the latent hydraulic property of the slag powder, which will be clearly seen by comparing the results in table 3 with the values in the Japanese Industrial Standard Specifications of various cements shown in table 4.

Second Series of Experiments

Next, another series of tests on the special kind of masonry cement, the method of manufacture of which was proposed by the author, were carried out. The testing method is similar to that in the above first-series experiments, and the results are tabulated in tables 5 and 6.

TABLE 2. *Mixing ratio, fineness, and chemical compositions of masonry cement samples*

(Percent)

	Sample A–1	Sample A–2	Market Sample
Mixing ratio			
Slag (1) or (2)	Slag (2) 80	Slag (1) 60	------
Slaked lime (1)	10	20	------
Fly ash (1)	10	20	------
Sieve fineness (residue)			
ASTM 50 meshes/in	0.2	0.2	0.1
70 meshes/in	.4	.5	.3
100 meshes/in	1.0	.9	.6
150 meshes/in	2.4	2.4	1.4
200 meshes/in	3.5	4.0	2.6
Chemical composition			
Loss on ignition	2.04	6.71	17.00
Insoluble residue	8.58	18.25	6.54
SiO_2	26.78	19.13	12.26
Al_2O_3	15.90	10.57	3.33
Fe_2O_3	.90	1.72	1.60
MnO	.66	1.13	------
CaO	38.47	38.32	57.26
MgO	3.42	3.32	1.74
SO_3	.08	.31	.75

TABLE 3. *Setting time of neat cement and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample	Mixing solution		Flow table value	Setting time test			Bending strength (kg/cm^2)			Compressive strength (kg/cm^2)		
	Kind	Amount		Amount of water	Initial	Final	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
		Percent	*Percent*	*Percent*	*hr-min*	*hr-min*						
A–1	Fresh water	60	200	34	5–01	11–23	9.2	20.6	13.9	25	64	61
	2.5% NaOH	63	204	34.2	1–13	2–34	33.6	39.5	14.8	55	139	139
	5% NaOH	63	203	34.6	1–12	2–55	21.8	50.5	40.3	138	176	183
	10% NaOH	65	193	35.5	0–56	1–56	30.1	60.2	57.4	260	310	315
	5% Na_2CO_3	64	163	------	Quick setting		19.6	38.2	32.0	65	93	88
	10% Na_2CO_3	65	153	------	(Not examined)		20.5	51.3	46.5	185	207	212
A–2	Fresh water	60	206	35	5–05	11–45	8.4	19.9	21.4	43	91	126
	5% NaOH	60	180	35.8	2–02	3–40	25.6	51.9	25.7	106	139	143
	10% NaOH	60	169	36.5	1–17	2–36	30.8	56.9	41.5	278	329	372
	5% Na_2CO_3	65	193	43	1–12	3–10	18.1	39.1	30.7	68	99	43
Market sample	Fresh water	60	177	36.5	2–17	3–43	21.7	38.5	43.9	117	158	173

TABLE 4. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar in the Japanese Industrial Standard Specifications*

Kind of cement	Mixing medium	Amount	Flow table	Setting time test			Bending strength (kg/cm^2)			Compressive strength (kg/cm^2)		
				Amount water	Initial	Final	7 days (in water)	28 days (in water)	28 days (in air)	7 days (in water)	28 days (in water)	28 days (in air)
		Percent	*Percent*	*Percent*	*hr-min*	*hr-min*						
Common portland cement	Fresh water	65	200	------	$>$1–00	$<$10–00	$>$25	$>$36	------	$>$90	$>$200	------
Rapid-hardening portland cement	do	65	200	------	$>$1–00	$<$10–00	$>$40	$>$60	------	$>$180	$>$280	------
Moderate-heat portland cement	do	65	200	------	$>$1–00	$<$10–00	$>$20	$>$30	------	$>$70	$>$150	------
Portland blast-furnace cement	do	65	200	------	$>$1–00	$<$10–00	$>$25	$>$36	------	$>$90	$>$200	------
Portland pozzolan cement	do	65	200	------	$>$1–00	$<$10–00	$>$25	$>$36	------	$>$90	$>$180	------
Miscellaneous-use cement [a]	do	65	200	------	------	$<$24–00	$>$10	$>$18	------	$>$30	$>$80	------
Slag-lime cement [a]	do	65	200	------	------	$<$24–00	$>$10	$>$18	------	$>$30	$>$80	------
Masonry cement (proposed by Nagai).[b]	do	65	200	------	------	$<$24–00	$>$12	$>$20	------	$>$40	$>$100	------

[a] Now out of use.
[b] Now not determined.

TABLE 5. *Chemical compositions of raw materials*

[Percent]

	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Basicity [b] (1)	Basicity [b] (2)	Fineness Residue on 0.088mm (88μ) sieve
Slag (3)	0.76	32.01	15.29	0.35	43.83	5.80	2.08	1.30	0 (all pass)
Slag (4)	.80	33.35	13.23	.45	46.25	5.37	1.93	1.32	0 (all pass).
Slaked lime (2)	21.08	1.14	.48	.18	50.37	26.84	-----	-----	0 (all pass).
Fly ash (1)	.34	60.72	22.15	8.63	3.64	1.04	-----	-----	2
Silica residue [a]	11.36	83.76	1.12	.81	.28	.08	-----	-----	0 (all pass).

[a] Residue from high pressure sulfur refinery plant.

[b] Basicity of slag (1): $(CaO+MgO+Al_2O_3)/SiO_2$; (2): $(CaO+MgO+1/3Al_2O_3)/(SiO_2+2/3Al_2O_3)$.

These masonry cement samples were also tested as to their properties of setting time and strength by the same methods as in the first series in table 3, and tabulated in table 7.

Some points can be clearly seen from these results: (1) these masonry cements have short setting times and high early strengths not less than the strength of common portland cement and other various mixed portland cements shown in table 4 (Japanese Industrial Standard Specifications), (2) the accelerating action of dilute NaOH solution is much better than that of dilute Na_2CO_3 solution, the results being quite similar to those already shown in table 3, (3) very large amounts (75–80 percent) of granulated slag, accelerated

TABLE 6. *Mixing ratios and chemical compositions of masonry cement samples*

[Percent]

	A-series			B-series			C-series	D-series	Market sample [b]
	A–70	A–75	A–65	B–70	B–75	B–65	C–80	D–60	
Mixing ratios									
Slag (3) or (4)	(3) 70	(3) 75	(3) 65	(4) 70	(4) 75	(4) 65	(2) 80	(1) 60	Unknown
Slaked lime (1) or (2)	(2) 30	(2) 10	(2) 10	(2) 30	(2) 10	(2) 10	(1) 10	(1) 20	
Silica residue	-----	15	25	-----	15	25	10	20	
Chemical composition									
Insoluble residue	-----	-----	-----	-----	-----	-----	8.58	18.25	6.54
Loss on ignition	6.84	4.37	5.43	6.87	4.40	5.46	2.04	6.71	17.00
SiO_2	22.81	36.69	41.88	23.89	37.85	42.84	26.78	19.13	12.26
Al_2O_3	10.84	11.69	10.27	9.40	10.14	8.93	15.90	10.87	3.33
Fe_2O_3	.30	.40	.45	.37	.48	.51	.90	1.72	1.60
CaO	45.79	37.95	33.59	47.49	39.77	35.16	38.47	38.32	57.26
MgO [a]	12.11	7.04	6.47	11.91	6.72	6.19	5.42	3.32	1.74

[a] Large MgO content is due to slaked lime in table 5 (dolomitic slaked lime, so-called dolime).

[b] This market sample of masonry cement was tested for fineness and strengths, as shown in tables 2 and 3.

TABLE 7. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample	Mixing solution	Setting time test			Flow test		Bending strength (kg/cm^2)				Compressive strength (kg/cm^2)			
		Amount of solution	Initial	Final	Amount of solution	Flow	3 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)	3 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
A-series:		*Percent*	*hr.-min.*	*hr.-min.*	*Percent*	*Percent*								
A–70	Fresh water	35.0	5–35	10–40	60	169	6.7	11.4	25.4	17.2	26	53	80	80
A–70	5% NaOH	34.9	2–12	5–05	60	169	23.0	23.5	30.9	24.3	46	56	81	89
A–70	10% NaOH	34.9	1–41	3–16	60	169	32.5	32.3	37.0	31.6	105	128	213	194
A–70	15% NaOH	34.7	1–12	2–50	60	169	30.1	24.9	40.3	18.3	89	102	163	159
A–75	10% NaOH	30.6	1–02	3–23	60	169	20.6	22.9	30.0	-----	61	91	126	-----
A–65	10% NaOH	34.3	1–45	4–25	60	169	14.3	17.6	21.8	-----	50	69	86	-----
B-series:														
B–70	Fresh water	35.5	3–55	8–35	60	169	6.9	11.0	19.9	13.5	42	86	130	133
B–70	5% Na_2CO_3	37.4	3–55	4–55	60	169	22.9	24.2	39 8	25.6	54	100	140	155
B–70	10% Na_2CO_3	43.3	1–30	2–30	60	169	26.8	30.7	53.6	30.9	111	148	211	323
B–75	10% Na_2CO_3	40.3	0–25	3–02	60	169	-----	6.4	7.0	-----	-----	18	21	-----
B–65	10% Na_2CO_3	40.3	0–40	3–37	60	169	-----	4.3	6.2	-----	-----	16	19	-----
C-series:														
C–80	Fresh water	34.0	5–01	11–23	60	200	-----	9.2	20.6	13.9	-----	25	64	61
C–80	2.5% NaOH	34.2	1–13	2–34	63	204	-----	33.6	39.3	34.8	-----	55	139	139
C–80	5% NaOH	34.1	1–12	2–35	63	203	-----	21.8	50.5	40.3	-----	138	176	183
C–80	10% NaOH	35.5	0–56	1–56	65	193	-----	30.1	60.2	57.4	-----	260	310	315
C–80	5% Na_2CO_3	-----	-----	-----	64	163	-----	19.6	38.2	32.0	-----	65	93	88
C–80	10% Na_2CO_3	-----	-----	-----	65	155	-----	20.8	51.3	46.5	-----	185	207	212
D-series:														
D–60	Fresh water	35.0	5–05	11–45	60	206	-----	8.4	19.9	21.4	-----	43	91	125
D–60	5% NaOH	35.8	2–03	3–40	60	180	-----	25.6	51.9	25.7	-----	106	139	142
D–60	10% NaOH	36.5	1–27	2–36	60	169	-----	30.8	56.9	41.5	-----	278	329	372
D–60	5% Na_2CO_3	43.0	1–12	3–10	65	193	-----	18.1	39.1	30.7	-----	68	94	91

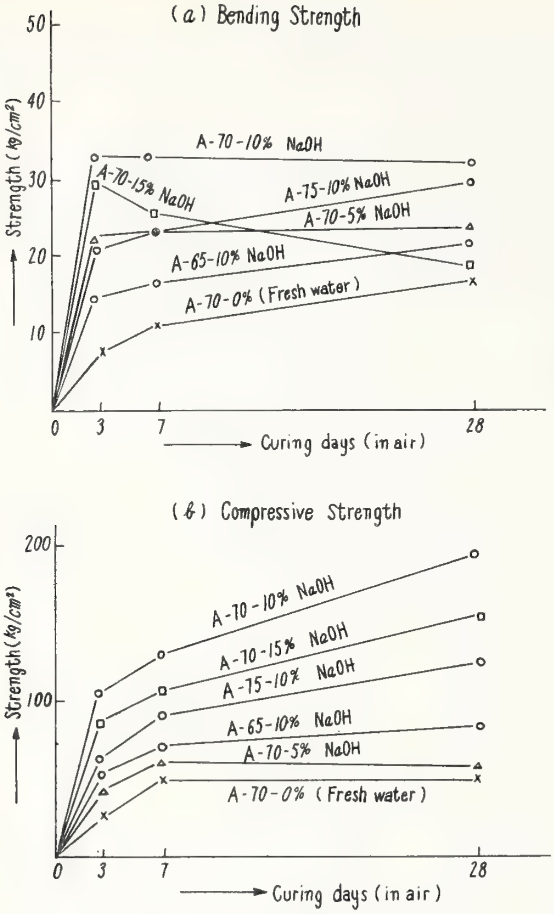

Figure 1. *Bending and compressive strengths of masonry cement mortars, series A.*

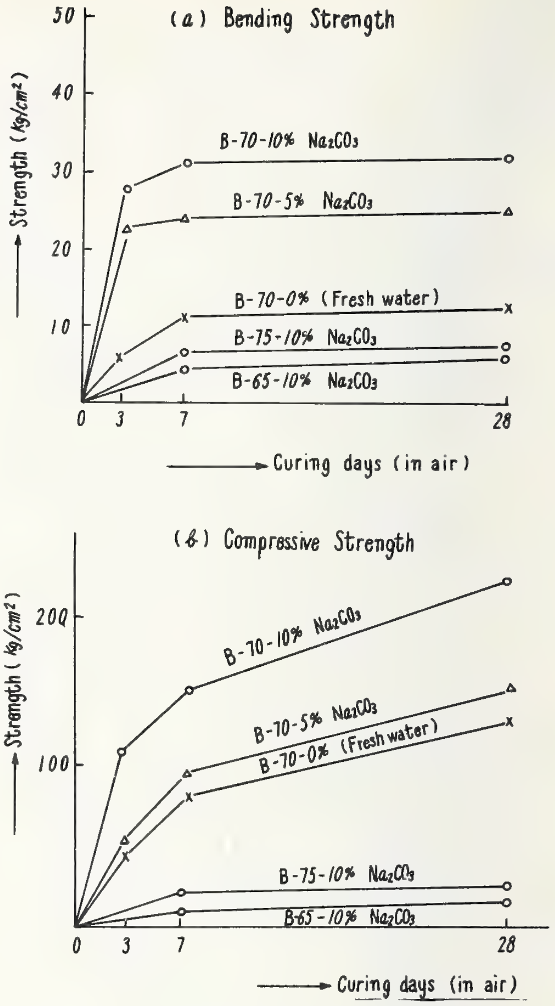

Figure 2. *Bending and compressive strengths of masonry cement mortars, series B.*

only by dilute NaOH solution, can be used with good results in respect to quick setting time and high early strength, (4) these early-setting and high-strength results obtained with acceleration by dilute NaOH solution are about 3–4 times greater than those obtained with fresh water, etc. The results of the strength tests are shown in figures 1–4. In all the figures, the curves of strengths obtained with fresh mixing water are all low; and in figure 2, the strengths obtained with dilute Na_2CO_3 solution are clearly lower than those obtained with fresh water.

Third Series of Experiments

Further tests were carried out in the same way on the special masonry cement, using a large amount of granulated slag mixed with slaked lime and siliceous admixture and mixing with dilute (1–5 percent) NaOH solution, the accelerating effect of which on the latent hydraulic property of granulated slag was clearly determined in the foregoing experiments (the first and second series).

In the third series of experiments, nine kinds of masonry cement samples were prepared by using slag, slaked lime, and siliceous admixture. The chemical compositions of these raw materials are tabulated in table 8. In this series, slaked limes (5) and (6) were obtained from a carbide acetylene-producing plant (by dry process), and natural pozzolanic materials were used instead of the siliceous residue from a pressure-steam sulfur refinery. One of the pozzolans is the famous high-silica (over 92 percent in the alkali-soluble state) material, nearly all soluble in dilute NaOH solution, obtained from the acidic hot spring, Beppu, in the Oita Prefecture.

Table 8. *Chemical compositions of raw materials*

[Percent]

Kind of sample	Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Sulfide sulfur
Slag (5)	0.45	0.24	32.19	18.28	0.77	41.26	6.23	0.97
Slag (6)	.71	.59	31.92	19.53	1.33	38.70	5.06	.96
Slag (7)	+.31[a]	.15	32.14	18.02	1.23	40.30	6.92	1.47
Slaked lime (5)	27.36	.92	1.51	1.14	1.14	69.02	.04	.50
Slaked lime (6)	23.47	.80	1.82	.80	.80	72.93	.54	.36
Fly ash (2)	3.78	------	55.33	28.57	5.83	4.65	1.28	------
Natural pozzolan (1)	6.57	------	58.37	20.76	7.39	2.57	2.97	------
Natural pozzolan (2)	3.94	------	92.01	2.30	.49	.07	------	------

[a] Slag gained weight.

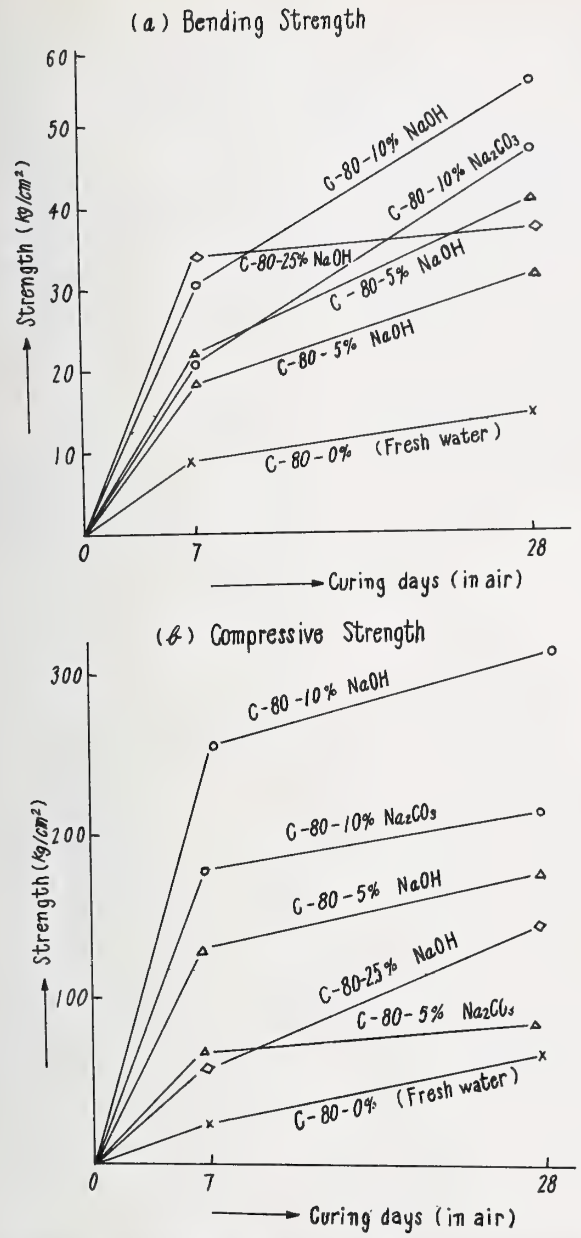

FIGURE 3. *Bending and compressive strengths of masonry cement mortars, series C.*

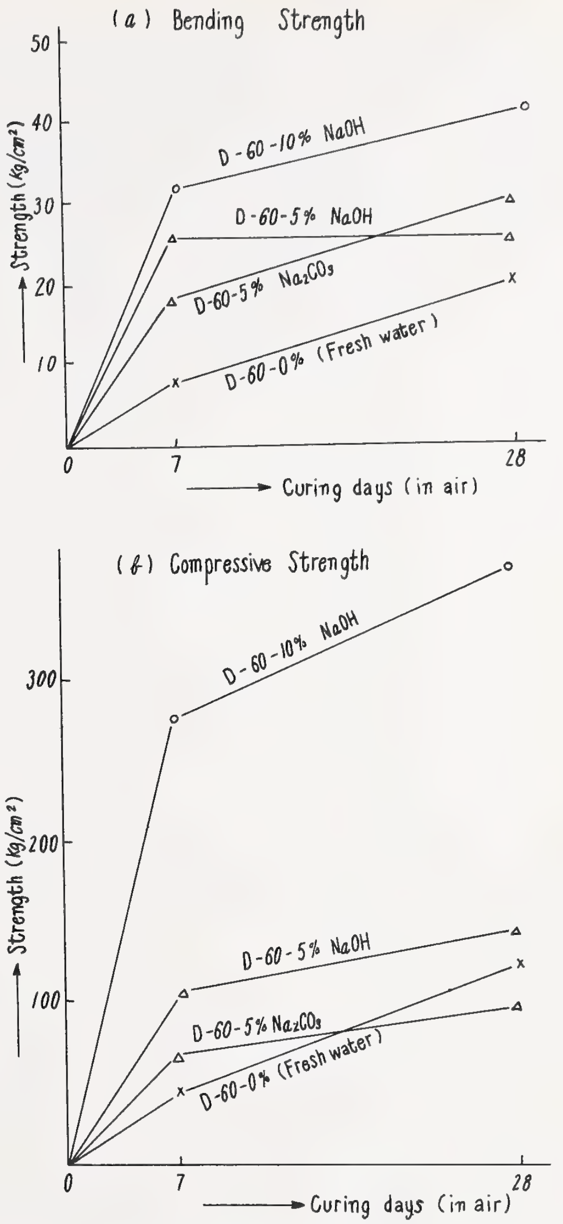

FIGURE 4. *Bending and compressive strengths of masonry cement mortars, series D.*

The mixing proportions for making the masonry cement samples, the finenesses, and the chemical compositions of the prepared cement samples are tabulated in table 9.

From the chemical compositions, it can be easily seen that these series of prepared cement samples contain large amounts of insoluble residue and, on the contrary, small amounts of SiO_2 and CaO, owing to the large mixing ratio (30 percent) of natural or artificial siliceous pozzolanic matter.

Next, these prepared cement samples were examined or tested in the same way as in the first and second series of experiments, with the comparable good results tabulated in table 10. In the present case, the accelerating alkaline solution was limited to dilute NaOH (1, 3, or 5 percent) solution, and the water-cement ratio (w/c), or in this case, the water solution-cement ratio, was limited to 0.60, so that the amount of alkali (Na_2O) was only about 0.37, 1.2, or 1.8 percent. The accelerating action of this alkaline solution on the setting time and the strengths is weak with the 1-percent solution and is adequate with the 3-percent solution. This amount of alkali is the important point for the masonry cement mortar in respect to various properties of soundness, expansion or contraction, surface hardness, efflorescence, etc. Some of these points were preliminarily examined in the present experiments, e.g., the soundness on setting and hardening of the

TABLE 9. *Mixing ratio of raw materials, fineness, and chemical compositions of masonry cement samples*

[Percent]

Designation of cement sample	Mixing ratio			Fineness (88-μ sieve residue)	Chemical composition (%)						
	Slag (No.)	Admixture (No.)	Slaked lime (No.)		Loss on ignition	Insol. res.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
A	(5):50	(1):30—Silica residue	(1):20	3.2	6.19	27.29	18.06	8.80	0.51	34.64	3.31
B	(5):50	(2):30—Fly ash	(1):20	2.8	6.51	22.48	18.59	10.86	1.04	35.40	3.55
C	(6):50	(2):30—Pozzolan	(5):20	3.2	7.53	24.62	15.52	13.24	.93	33.74	3.67
D	(7):50	(1):30—Fly ash	(5):20	3.2	4.54	26.23	16.78	10.74	1.94	34.51	2.97
E	(7):50	(3):30—Pozzolan	(5):20	3.8	7.40	23.91	19.88	9.93	1.56	34.07	3.03
F	(6):60	(2):30—Fly ash	(5):10	2.8	2.89	24.05	20.70	18.63	1.84	31.26	4.07
G	(6):60	(2):30—Pozzolan	(5):10	2.8	4.85	21.24	22.16	12.79	2.51	30.72	4.48
H	(7):60	(1):30—Fly ash	(5):10	2.6	1.97	25.46	24.12	11.24	2.45	31.14	3.48
I	(7):60	(3):30—Pozzolan	(6):10	3.6	3.65	20.54	27.10	9.74	1.50	32.28	3.68

TABLE 10. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample		Mixing solution	Setting time tests			Flow test		Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
			Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 day (in air)	7 days (in air)	28 days (in water)	28 days (in air)
			Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
A	a	Fresh water	39.2	5-51	12-02	60	185	12.3	32.2	29.9	23	88	97
	b	1% NaOH	40.0	3-53	7-17	60	181	24.3	40.4	39.5	60	121	112
	c	3% NaOH	40.2	1-52	4-03	60	169	24.1	42.1	38.6	60	85	88
B	a	Fresh water	38.0	4-55	13-17	60	208	8.6	27.8	24.7	10	78	84
	b	1% NaOH	39.0	3-51	7-16	60	202	22.0	46.3	34.7	85	170	146
	c	3% NaOH	39.5	2-27	4-24	60	201	22.3	49.3	28.0	72	99	98
C	a	Fresh water	33.8	10-28	19-53	60	183	9.9	26.1	16.8	20	71	66
	b	1% NaOH	34.0	5-18	9-53	60	176	25.4	43.8	34.6	75	128	122
	c	3% NaOH	34.0	1-53	3-48	60	176	37.8	42.6	33.3	57	82	80
D	a	Fresh water	32.0	5-04	11-32	60	230	10.7	22.6	20.3	19	56	64
	b	1% NaOH	34.0	4-19	6-07	60	224	17.2	39.1	31.8	71	126	120
	c	3% NaOH	34.0	1-37	3-00	60	222	31.9	45.4	37.1	70	102	96
	d	5% NaOH	34.2	1-17	2-06	60	215	28.0	60.5	47.1	119	170	166
E	a	Fresh water	40.0	4-38	8-46	60	165	15.1	43.8	34.1	64	89	67
	b	1% NaOH	40.0	3-22	6-23	60	160	17.6	42.2	35.9	89	156	168
	c	3% NaOH	42.5	1-36	3-00	60	159	18.9	49.8	40.8	67	104	102
	d	5% NaOH	42.5	1-10	2-10	60	154	31.8	58.7	44.3	131	183	179
F	a	Fresh water	32.5	11-48	22-14	60	231	8.9	21.7	21.5	14	53	51
	b	1% NaOH	33.3	8-18	12-15	60	230	22.5	40.8	35.6	60	120	105
	c	3% NaOH	33.7	4-45	5-42	60	230	24.1	48.5	38.1	66	101	90
G	a	Fresh water	32.0	8-17	20-09	60	222	12.6	29.4	23.7	30	85	65
	b	1% NaOH	32.5	6-00	10-06	60	206	26.2	37.7	25.2	47	122	120
	c	3% NaOH	32.5	1-51	4-18	60	205	25.4	35.7	32.2	64	90	87
H	a	Fresh water	30.0	5-28	8-33	60	230	12.4	14.1	20.0	49	72	64
	b	1% NaOH	31.5	4-47	5-51	60	228	12.0	38.2	25.8	69	122	120
	c	3% NaOH	31.5	2-17	3-22	60	225	24.6	44.6	30.8	76	126	125
	d	5% NaOH	31.7	2-12	3-05	60	222	39.9	64.6	37.5	143	198	193
I	a	Fresh water	40.0	4-27	8-57	60	172	19.6	32.5	26.9	60	90	90
	b	1% NaOH	41.0	3-37	6-43	60	170	21.4	30.6	28.6	75	121	120
	c	3% NaOH	42.0	1-58	4-11	60	168	24.7	37.4	31.0	66	122	122
	d	5% NaOH	42.0	1-28	2-55	60	165	35.0	46.4	38.0	135	183	187

neat cement paste, by the pat test on boiling for 3 hr or curing in water for 28 days, proved to be fully as satisfactory as that of common portland cement. The other tests will be reported in the next series of experiments.

Fourth Series of Experiments

Further tests were carried out in the same way, by using fly ash, slaked lime, or calcined gypsum as the mixing materials added to the principal slag component of the masonry cements. Another kind of masonry cement sample was prepared by mixing finely powdered dolomite with portland cement in various proportions. The chemical composition and finenesses of these raw materials were determined and tabulated in table 11.

In the present series, calcined gypsum was used instead of pozzolanic admixtures such as siliceous matter or fly ash, and another kind of masonry cement samples, prepared by mixing intimately portland cement with fine dolomite powder, was tested and compared with other masonry cement samples. These cement samples are tabulated in table 12, with their mixing ratios, finenesses, and chemical compositions.

Then, as shown in table 13, the special accelerating agent, dilute Na_2SO_4 solution, was used with or without dilute NaOH solution, and good results were obtained. Both initial and final setting times of neat cement paste were considerably accelerated by mixed 1.5-percent NaOH and 1.5-percent Na_2SO_4 solution or 3 percent NaOH solution alone, but 3-, 5-, or 10-percent Na_2SO_4 solution alone did not accelerate the setting time. But the 1:2 cement-sand mortar was quickly hardened, and both bending and compressive strengths were good with either NaOH (3 percent) or Na_2SO_4 solution. This action by dilute Na_2SO_4 solution causing slower setting, but very quick hardening, of mortar is very convenient for plastering of masonry cement mortar on concrete, wire, or wood lath for walls or ceilings, etc.

Another kind of masonry cement obtained from portland cement and finely powdered dolomite (in proportions of 70:30 or 50:50) has slower setting and weaker mortar strength with increasing proportion of dolomite.

TABLE 11. *Fineness and chemical compositions of raw materials*

[Percent]

Kind of sample	Fineness (residue on 88μ-sieve)	Chemical composition							
		Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Slag (8)	2.0	1.83	0.34	32.24	16.35	0.97	38.51	6.97	1.25
Fly ash (1)	2.0	.34	--------	60.72	22.15	8.63	3.64	1.04	--------
Slaked lime (6)	All pass	23.47	.80	.82	.80	.80	72.94	.54	.36
Portland cement (1)	3.6	1.78	.33	22.60	4.57	2.97	64.98	1.26	1.33
Dolomite powder (1)	5.4	46.78	.48	.03	.47	.47	34.57	18.04	--------
Calcined gypsum (1)	All pass	--------	2.93	2.93	.29	.50	39.62	.19	56.65

TABLE 12. *Mixing ratio, fineness, and chemical compositions of masonry cement samples*

[Percent]

Designation of sample	Mixing Ratios			Fineness (88μ-sieve residue)	Chemical compositions							
	Slag	Fly ash or calcined gypsum	Slaked lime		Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
S_1	(8) 60	Fly Ash (1) 20	(6) 20	3.2	4.05	18.09	19.59	10.44	0.87	38.45	4.72	------
S_2	(8) 60	Fly Ash (1) 30	(6) 10	3.2	2.01	25.53	24.03	11.20	1.50	31.14	3.20	------
G_1	(8) 85	Calcined Gypsum (1) 10.	(5) 5	2.0	2.73	0.53	27.54	13.94	0.87	40.34	6.00	5.72
G_2	(8) 87	Calcined Gypsum (1) 8.	(5) 5	2.2	2.70	.50	27.50	13.90	.85	40.40	5.95	4.13
G_3	(8) 94	Calcined Gypsum (1) 0.	(5) 6	2.0	2.76	.45	27.52	13.93	.80	40.70	6.22	------
P_{100}	Portland cement (1) 100.	------	Dolomite powder (1) 0.	3.8	1.78	.33	22.60	4.57	2.97	64.98	1.26	1.33
P_{70}	Portland cement (1) 70.	------	Dolomite powder (1) 30.	4.0	15.28	.37	15.82	3.27	2.15	55.85	6.29	.93
P_{50}	Portland cement (1) 50.	------	Dolomite powder (1) 50.	4.5	24.23	.40	11.32	2.40	1.60	49.77	9.65	.66

TABLE 13. *Setting time and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Designation of sample	Mixing solution	Setting time test			Flow test		Bending strength (kg/cm ²)			Compressive strength (kg/cm ²)		
		Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
		Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
S_1	Fresh water	32.0	7–31	17–23	60	224	4.1	7.0	10.0	4	11	12
	1.5% NaOH+1.5% Na_2SO_4.	32.5	1–00	2–10	60	205	16.6	36.1	36.0	66	130	131
	3% NaOH	32.5	1–49	4–01	60	210	17.9	40.3	39.0	68	115	110
	3% Na_2SO_4	32.5	3–35	5–38	60	190	26.6	40.0	38.5	71	104	102
S_2	Fresh water	30.0	8–59	16–27	60	262	----------	6.4	8.5	----------	6	6
	1.5% NaOH+1.5% Na_2SO_4.	30.8	3–55	5–26	60	260	28.0	37.5	36.1	85	134	123
	3% NaOH	31.0	2–05	4–18	60	260	27.0	41.5	39.1	77	120	108
	3% Na_2SO_4	31.2	9–27	11–55	60	260	33.5	40.2	41.2	79	104	103
	5% Na_2SO_4	32.0	9–07	12–13	60	254	25.9	47.6	44.0	124	169	161
	10% Na_2SO_4	33.0	9–14	11–48	60	250	29.6	70.8	61.0	138	216	211
G_1	Fresh water	30.0	10–20	15–50	60	240	40.1	62.5	57.4	135	229	221
G_2	3% Na_2SO_4	30.5	8–15	14–00	60	238	28.0	58.6	56.8	80	170	163
G_3	10% Na_2SO_4	33.0	8–05	10–45	60	205	28.7	93.1	82.1	287	390	375
P_{100}	Fresh water	28.0	2–02	3–03	60	250	47.1	69.5	70.8	226	397	415
P_{70}	Fresh water	25.8	2–12	3–14	60	240	37.6	55.3	47.7	151	228	187
P_{50}	Fresh water	24.5	2–28	3–44	60	240	24.3	34.9	38.3	82	124	116

The surface hardness of hardened mortar was tested by the degree of penetration of a modified Vicat tester. The results are tabulated in table 14, by comparison of the penetration depths on the hardened test pieces, cured for 28 days in air or in water, and it is observed that the surface hardness of masonry cement mortar is nearly uniform in the case of 28 days of water curing, but a little softer in the case of 28 days of air curing.

Next, the efflorescence was examined first by qualitative observation of white stain or white fibrous salt deposit. This efflorescence was wiped off and the specimen cured further to observe any further formation of the white efflorescence. The test pieces mixed with Na_2SO_4 solution were a little more stained by the white efflorescence. This test was carried out on 4- x 4- x 16-cm prismatic test pieces, cured 7 days in air and then dipped vertically half way (about 8 cm) in water. This efflorescence test was further used in the following series of experiments.

TABLE 14. *Surface-hardness testing of masonry cement mortar*

Kind of sample	Mixing solution	Penetration depth mm	
		28 days (in water)	28 days (in air)
S_1	Fresh water	0.1	0.2
	1.5% NaOH+1.5% Na_2SO_4	.1	.5
	3% NaOH	.1	.2
	3% Na_2SO_4	.1	.5
S_2	Fresh water	.1	.2
	1.5% NaOH+1.5% Na_2SO_4	.1	.5
	3% NaOH	.1	.2
	3% Na_2SO_4	.1	.5
	5% Na_2SO_4	.1	.5
	10% Na_2SO_4	.1	.5
G_1	Fresh water	.1	2.0
G_2	3% Na_2SO_4	.1	.5
G_3	10% Na_2SO_4	.1	.5
P_{100}	Fresh water	.1	.1
P_{70}	Fresh water	.1	.1
P_{50}	Fresh water	.1	.1

Fifth Series of Experiments

In this series of experiments, the purpose was to determine whether special cement samples produced by mixing granulated slag, slaked lime, and electric treater dust from a cement manufacturing plant are suitable for use for masonry cement mortar. The object of using cement dust from an electric dust-catching treater for mixing in the special masonry cement is, (1) to replace the dilute Na_2SO_4 solution, for accelerating the latent hydraulic property of slag in the foregoing experiments, by the Na_2SO_4 and K_2SO_4 contained in the cement dust (about 3–5 percent of Na_2SO_4 and 2–4 percent of K_2SO_4), (2) to make use of the weak hydraulic property of cement dust, (3) to use the free lime contained in the cement dust (about 5–15 percent), instead of the slaked lime used in the foregoing experiments, and (4) to use the free silica and alumina from the calcined clay part of the cement raw mixture (about 5–10 percent SiO_2 and 2–4 percent Al_2O_3 in the soluble state), instead of the pozzolanic admixture used in the foregoing experiments.

These raw materials for making the special series of masonry cement samples were analyzed, and the results are tabulated in table 15. The samples of electric-treater cement dust were collected from various cement plants using dry or wet processes, and observed to be quite different in content of alkali (Na_2O and K_2O) and CaO (especially free CaO) with differences in raw materials, burning process, dust-catching plant, etc.

The cement samples were prepared by using these raw materials in the proportions shown in table 16 and tested for fineness and chemical composition.

Next, these cement samples were tested in the same way, as to their setting times of neat cement paste and the bending and compressive strengths of 1:2 cement-sand plastic mortar, by the method in the Japanese Industrial Standard Specification (JIS R 5201). The data are given in table 17.

From these results the following points were observed, (1) Na_2SO_4 powder can be added to the cement and mixed with water, instead of the dilute Na_2SO_4 solution in the foregoing experiments, and nearly equal results obtained, so that it can be assumed that the electric-treater cement dust containing both Na_2SO_4 and K_2SO_4 will be

TABLE 15. *Chemical compositions of slag, slaked lime, and cement dust*

[Percent]

Kind of sample	Loss on ignition	Insol. residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Fineness (88-μ-sieve residue)
Slag (8)	1.83	0.34	32.24	16.35	0.97	38.51	6.97	0.07	------	------	2.0
Slag (9)	.51	.13	31.73	18.30	.76	38.47	8.30	.12	------	------	1.2
Slag (10)	+.15 [a]	.25	31.24	17.09	.61	38.61	7.76	.08	------	------	1.8
Slag (11)	------	.22	31.78	10.03	.73	38.20	6.97	.07	------	------	.6
Fly ash (1)	.34	------	60.73	22.15	8.63	3.64	1.04	------	------	------	2.0
Fly ash (3)	5.23	------	53.87	27.31	6.52	2.75	1.28	------	------	------	2.9
Slaked lime (6)	23.47	.80	.82	.80	.80	72.93	.54	------	------	------	(All pass)
Slaked lime (7)	26.97	1.13	.83	.96	.12	68.30	.25	------	------	------	do
Slaked lime (8)	28.06	3.37	3.37	1.43	.67	66.17	.15	------	------	------	6.8
Slaked lime (9)	26.90	.69	1.23	.51	.51	67.34	.55	------	------	------	(All pass)
Cement Dust (1)	16.41	------	14.35	4.37	1.53	35.41	1.03	13.16	4.48	3.60	8.8
Cement Dust (2)	13.42	------	18.77	5.36	1.65	52.37	1.21	3.91	2.00	2.38	2.0
Cement Dust (3)	9.38	------	24.02	6.83	2.78	45.59	1.60	5.05	2.07	2.28	2.3
Cement Dust (4)	27.36	------	15.85	3.41	2.75	40.46	1.63	2.77	2.05	1.89	2.5

[a] Gain in weight.

Table 16. *Mixing ratio, fineness, and chemical composition of cement samples*

[Percent]

Series designation	Mixing ratio			Fineness (88-μ-sieve residue)	Chemical composition									
	Slag	Fly ash or dust	Slaked lime		Loss on ignition	Insol. residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
A	(8) 60	Fly ash (1) 30	(6) 10	3.3	2.01	25.55	24.03	11.20	1.50	31.14	3.20	------	------	------
B	(10) 60	Fly ash (1) 20	(7) 20	3.0	5.74	18.15	18.15	12.84	.70	38.88	5.02	------	------	------
C-1	(9) 50	Dust (2) 50	---------	2.2	6.99	4.70	21.32	11.86	1.57	45.56	4.47	1.19	1 05	0.65
C-2	(8) 50	Dust (1) 50	---------	4.9	9.36	3.61	19.47	11.39	1.27	36.91	3.88	6.80	4.47	2.33
C-3	(8) 60	Dust (1) 40	---------	3.7	7.65	2.81	22.46	13.14	1.19	37.27	4.59	5.25	3 43	1.09
C-4	(8) 50	Dust (1) 30	(8) 20	5.6	11.51	2.21	18.61	11.01	1.09	43.06	3.78	4.02	2.62	1.36
C-5	(8) 60	Dust (1) 20	(8) 20	4.5	10.07	1.51	21.93	12.48	1.03	43.31	4.38	2.70	1.76	.92
D-1	(11) 50	Fly ash (3) 30	(9) 20	2.2	5.53	---------	34.57	16.45	3.22	33.74	3.93	1.10	------	------
D-2	(11) 60	Fly ash (3) 30	(9) 10	2.7	2.81	---------	37.95	11.27	3.76	37.46	3.87	1.42	------	------

Table 17. *Setting time, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Series of samples	Salt	Mixing medium	Setting time			Flow test		Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
			Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
			Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
A	2% Na_2SiF_6	Fresh water	35.0	4–05	7–15	65	185	8.8	24.4	12.7	8	74	95
	3% $Na_2O{\cdot}3SiO_2$	Solution	39.5	2–13	6–10	65	154	11.7	34.6	15.7	68	123	94
	2% Na_2SO_4	Fresh water	35.0	8–15	11–35	64	199	24.5	45.4	17.4	113	157	160
	2% $Na_2SO_4{\cdot}10H_2O$	do	32.5	9–25	11–45	63	206	15.4	49.6	22.3	75	145	126
	3% Na_2SO_4	Solution	36.0	7–50	10–45	65	182	20.0	44.6	24.7	95	148	186
C-1	---------	Fresh water	35.5	2–12	8–24	60	189	39.3	60.3	54.2	210	365	295
C-2	---------	do	36.0	2–50	6–30	60	177	22.1	40.3	44.3	21	222	253
C-3	---------	do	36.5	2–40	7–10	60	152	12.8	21.6	33.3	56	118	164
C-4	---------	do	35.0	2–30	6–55	60	155	54.6	57.8	33.9	144	165	167
C-5	---------	do	35.5	2–10	6–30	60	173	54.5	59.4	25.9	145	204	147

suitable for use as an admixture to masonry cement, (2) dilute water-glass solution (or $Na_2O{\cdot}3SiO_2$ solution) accelerates nearly as well as the dilute Na_2SO_4 solution (2–4 percent) used in the foregoing experiments, (3) the special cements prepared by mixing granulated slag (50–60 parts) with electric-treater cement dust (50–40 parts), or cement dust (30–20 parts) with about 20 parts of slaked lime, have moderate setting time of neat cement paste and remarkably quick and high strength of cement-sand plastic mortar. Thus, special masonry cement of good quality can easily and at very low cost be obtained by intimately mixing granulated slag with electric-treater cement dust with or without addition of slaked lime (as waste product from carbide acetylene-producing plant, better from the dry process than from the wet process). The addition and the amount of slaked lime depends on the amount of free lime contained in the cement dust, and, when the content of free lime is over about 15 percent and the total lime is over about 50 percent, the addition of slaked lime is not always necessary.

These mixed cements, composed of slag and cement dust, have remarkably good properties, as determined in the experiments, (1) moderate setting time, (2) superior rapid and high strength. Other points, (a) water-retention power, (b) efflorescence, (c) expansion or contraction, etc., will be further considered.

The test for efflorescence on mortar surface was carried out by the same method adopted in the foregoing series of experiments. Prismatic test pieces, 4 x 4 x 16 cm, for testing of bending and compressive strengths were also used for this efflorescence test, after 7 days curing in air, by dipping vertically halfway (about 8 cm) in water, and observing the degree of white stain and white flower-type salt efflorescence on the hardened mortar surface of the test piece in air. By these experiments, the following points were observed, (1) the test pieces of slag-cement dust cement mortar did not produce any efflorescence even after dipping in water for many weeks, (2) the addition of a large amount of cement dust (about 40–50 parts) as the important component of the masonry cement is very effective, which effect is perhaps because of the proper content of alkali sulfates (Na_2SO_4 and K_2SO_4) in the cement dust, (3) the efflorescence was not produced on the pieces which were wiped clean of efflorescence with a wet towel and then again dipped in water for many weeks.

Next, the water-retention power was tested by the method prescribed in the Japanese Industrial Standard Specifications for hydrated lime, gypsum, and dolomite plasters (JIS A 6902, 6903, and 6904), and the results shown in table 18 were obtained.

From these results, the following points are to be observed: (1) slag-lime (with 30 percent of fly ash) cements (D–1 and D–2) have high water-retention power, higher when made with dilute

Table 18. *Water retention power and plasticity of neat cement paste*

Designation of sample	Mixing solution		Water retention power (percent)			Plasticity Coefficient	
	Kind	Amount	After 2 min	After 4 min	After 6 min	10 °C	15 °C
		percent					
C–5	Fresh water	29.8	87.4	80.2	80.2	10.20	12.75
D–1	3% NaOH	29.3	87.3	86.6	86.5	9.96	12.45
D–1	3% Na_2SO_4	28.7	92.0	91.3	91.2	10.16	12.70
D–2	3% NaOH	30.3	86.8	86.1	86.1	10.72	13.40
D–2	3% Na_2SO_4	30.2	89.5	88.2	88.2	10.12	12.65

Na_2SO_4 solution than when made with dilute NaOH solution, and (2) slag-lime (with 20 percent of cement-dust) cement (C–5) has a little lower water-retention power. The water-retention power is remarkably affected by the fineness, porosity, water-soluble parts, etc., of the slag and admixing materials (lime, fly ash, cement electric-treater dust, etc.); among them the cement dust contains a fairly large amount of water-soluble alkali salts, and these salts have a large effect on the water-retention power. Next, the plasticity or viscosity of neat cement paste mixed with water (C–5), or with 3-percent NaOH or Na_2SO_4 solution (D–1 and D–2), shown in table 18, was tested and determined to be considerably greater than the limit value (not less than 7.5 at 15 °C) in the Japanese Industrial Standard Specifications of gypsum, lime, and dolomite plasters (JIS A 6902, 6903, and 6904).

The expansion or contraction, or cracking, and the surface hardness of hardened test pieces were systematically tested by the methods specified in the Japanese Industrial Standard Specifications above cited, on 1:2 or 1:3 cement-sand mortar, and good results were obtained, superior to those defined in the standards cited above.

Conclusion

The special masonry cement for use with concrete block, artificial slag brick or stone, etc., and surface mortaring of concrete and wire or wood lath, especially in Japan for fireproofing of wooden buildings, is a most important material for all building. It is said that about 1.5–2 million tons of cement per year is now used for this purpose, and it is a most important point to make a proper mortaring and masonry cement of low price.

The author has studied various kinds of cementing materials for many years, especially the special cement used for plastering which must have several important features, e.g., (1) low price, (2) a suitable setting time, (3) adequate strength, (4) good consistency or high plasticity, (5) low expansion or contraction and less cracking, (6) high water-retentive power, (7) superior surface hardness.

In the present paper, test results are reported for many kinds of special cements for mortaring and plastering, especially of the special cement of high content of water-granulated blast-furnace slag, mixed with various kinds of siliceous material and slaked lime from a lime hydrating plant or carbide acetylene-producing plant, and small amounts of alkali or alkali salt in solution or powder form, which is a most important matter for the accelerating of the weak latent hydraulicity of water-granulated slag.

The following are some of the most important points obtained from the various series of experiments.

(a) The cement is considerably cheaper than the ordinary cements, e.g., portland cement, portland blast-furnace cement, portland-pozzolan cement, portland fly-ash cement, etc., owing to the low cost of all component materials, (1) water-granulated blast-furnace slag, (2) natural pozzolan or artificial byproduct siliceous matter, (3) fly ash from fine-powdered coal-firing electric plants, (4) cement dust from dust-catching electric treaters, (5) waste slaked lime from lime hydrating plants or byproduct lime waste from carbide acetylene plants, (6) with or without (in the case of using cement dust) small amounts of alkali or alkali salt in dilute solution in the mixing water, or alkali salt in powder form for preliminary addition to cement.

(b) The large content of water-granulated blast-furnace slag as the main component gives the cement a weak hardening property, owing to the weak latent hydraulicity of granulated slag, which must be accelerated by adding a proper amount of slaked lime, and the excess of slaked lime must then be hydrated to calcium hydrosilicate $x\text{CaO}\cdot y\text{SiO}_2\cdot z\text{H}_2\text{O}$ by the active or soluble silica in the added pozzolanic siliceous matter of natural or artificial byproduct origin. The addition of fly ash is effective in increasing the plasticity, in decreasing the contraction or expansion, and in gradually developing over long periods the pozzolanic action characteristic of natural or artificial pozzolanic matter, etc.

(c) However, these special slag-lime cements are slow setting and low in strength, even with proper mixing of granulated blast-furnace slag, natural or artificial pozzolanic materials, and slaked lime. Thus, it is most important to accelerate the setting time and increase the strength by adding an affective accelerating agent. For this purpose, the addition of the proper small amount of alkali or alkali salt in dilute solution in place of the mixing water, or finely powdered alkali salt to the cement, is a most effective means of accelerating the setting and increasing the strength. The amount of alkali or alkali salt is very small, the amount necessary to accelerate the slow setting and weak strength of the special slag-lime cement being about 1–3 percent..

The cement dust from electric dust-catching plants, used for mixing (about 30–50 percent) with the cement as one of the main admixing components, is most effective for this purpose, owing to the following facts: (1) the content (about 2–5 percent) of both Na_2SO_4 and K_2SO_4 in the cement dust reacts as the accelerating agent above mentioned, (2) the content of free lime (about 10–18 percent) in the cement dust replaces slaked lime as one of the main components of the special slag-lime cement, (3) some calcium silicate, $m\mathrm{CaO}\cdot n\mathrm{SiO}_2$, of lower lime content contained in the dust, which was produced at the relatively lower temperature in the upper part of the cement rotary kiln, has a weak hardening property, which, even though very small, is effective in the cement, (4) the free silica and alumina, which were produced by calcining the clay part of the cement raw mixture in the upper part of the rotary kiln, react as siliceous admixtures replacing natural or artificial pozzolanic matter as above mentioned.

(d) The high-slag-content special slag-lime cement made by proper proportioning of water-granulated blast-furnace slag, slaked lime, natural or artificial siliceous pozzolanic matter, fly ash or cement dust, and a small amount of alkali or alkali salt, shows accelerated setting and increased strength and improvement in various properties needed for mortaring, plastering, and masonry uses, i.e., plasticity or consistency, water-retention power, decrease in expansion or contraction and cracking, decrease in efflorescence (especially by using cement dust), improved surface hardness, etc.

(e) For these purposes, the author for many years has studied many kinds of special slag-lime cement, especially for masonry, mortaring, and plastering uses, the provision of which is a most important problem in Japan for concrete, concrete block, wood or wire-lath building, etc. In Japan, there is now no marketable masonry cement, but some kinds of masonry cement are now being studied as to their marketable production, use for various purposes, and the official testing processes to be enacted in the near future as the Japanese Industrial Standard Specification.

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Paper VIII–S3. Blast-Furnace Cement in the USSR*

I. I. Kholin and S. M. Royak

Synopsis

The scientific basis for the use of slags in the manufacture of cement and practical means for improving the quality of blast-furnace cement are explained.

Nearly all kinds of slags derived from cast-iron, Bessemer, and Martin processing are used in the USSR in the manufacture of blast-furnace cements.

Broad studies of the composition, structure, and hydration process of blast-furnace slags have been made in the USSR. It is found that the activity of a blast-furnace slag depends on a number of factors such as its temperature when tapped from the furnace, its chemical composition, the method and rate of cooling, and the mineralogical composition resulting.

Blast-furnace cement is widely used in the USSR because of its various valuable properties such as high tensile strength, low water requirement, low heat of hydration, high corrosion resistance, low shrinkage, etc.

The relatively slow increase of strength of common blast-furnace cement in the early ages of hydration can be overcome by increasing the fineness. Superfine grinding makes it possible to manufacture a high-strength blast-furnace cement.

A method of manufacturing melted portland cements by the addition of lime and iron ore to molten slag in a specially designed converter has been worked out in the USSR.

Résumé

Cet exposé explique le principe scientifique pour l'utilisation des laitiers dans la production du ciment et les moyens pratiques d'améliorer la qualité du ciment de laitier de haut fourneau.

Presque toutes les sortes de laitiers de haut fourneau dérivés d'opérations de fonte sont utilisées à l'URSS dans la production des ciments de laitier de haut fourneau.

Des études étendues sur la composition, la structure et le procédé d'hydratation des laitiers de haut fourneau ont été faites en URSS. On a trouvé que l'activité du laitier du haut fourneau dépend d'un certain nombre de facteurs tels que la température de coulée de haut fourneau, la composition chimique, la méthode et la vitesse de refroidissement et la composition minéralogique qui en résulte.

Le ciment de laitier de haut fourneau est largement utilisé à l'URSS à cause de ses différentes propriétés valables, telles que la haute résistance à la traction, la faible exigence d'eau, la faible chaleur d'hydratation, la forte résistance à la corrosion, le faible retrait, etc.

L'accroissement relativement lent de la résistance du ciment de laitier de haut fourneau commun au début de l'hydratation peut être surmonté si on accroît la finesse. Un broyage extrêmement fin rend possible la fabrication d'un ciment de laitier de haut fourneau à haute résistance.

Une méthode a été développée à l'URSS qui permet la fabrication de ciments portland fondus au moyen d'une correction du laitier fondu dans un convertisseur spécialement construit.

Zusammenfassung

Die wissenschaftliche Grundlage der Verwendung von Schlacken in der Zementherstellung und das wirtschaftliche Verfahren für die Verbesserung der Qualität der Hochofenzemente werden beschrieben.

In der UdSSR werden beinahe alle Schlacken, die von Hochöfen, Bessemerbirnen, oder Martinöfen kommen, für die Anfertigung der Hochofenzemente verwendet.

Man hat in der UdSSR die Zusammensetzung, die Struktur und den Hydratationsprozeß der Hochofenschlacken gründlich studiert, und man hat herausgefunden, daß die Aktivität dieser Schlacken durch eine Anzahl Faktoren beeinflußt wird, wie zum Beispiel die Temperatur bei welcher der Hochofen angestochen wird, die chemische Zusammensetzung, die Kühlmethode und -geschwindigkeit, und die endgültige Mineralzusammensetzung.

Man benutzt die Hochofenzemente häufig in der UdSSR, da sie sehr wertvolle Eigenschafte, wie eine hohe Zugfestigkeit, einen geringen Bedarf an Anmachwasser, eine niedrige Hydratationswärme, eine hohe Korrosionsfestigkeit, ein kleines Schwindmaß usw. besitzen.

Die Festigkeitszunahme der gewöhnlichen Hochofenzemente vollzieht sich während der ersten Hydratationsstufen sehr langsam, aber dieser Nachteil kann durch ein Heraufsetzen der Feinheit beseitigt werden. Ein Ultrafeinmahlen bringt die Möglichkeit hervor, einen hochfestigen Hochofenzement herstellen zu können.

Man hat auch in der UdSSR ein Verfahren, in welchem geschmolzene Portlandzemente aus der geschmolzenen Schlacke in einer Spezialbirne hergestellt werden, ausgearbeitet. Man muß zu diesem Zwecke besondere Zuschläge in die Birne geben.

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The use of blast-furnace slags for making various building materials has been known in the USSR for almost a century. In 1865, soon after the quenching of slag had been invented and its hydraulic properties revealed, the production of wall stones made from the mixture of lime and slag was started. In the cities of Dniepropetrovsk and Krivoy Rog the first large buildings were erected by use of blast-furnace-slag concrete in the last decade of the 19th century. Some time later, in 1913–1914, there was constructed in Dniepropetrovsk a works producing blast-furnace cement—the first one in Russia. At about that time the production of blast-furnace cement was started in Tula (Kosogorsk steel-works).

Despite the positive results of numerous tests and the accumulation of practical experience in using blast-furnace slag for construction, there passed some five years (1911–1916) between the issuing of technical specifications for this cement and its official introduction in concrete and reinforced-concrete constructions.

During the last 30 years the industry of cement and blast-furnace cement in the USSR showed a steep increase. Large plants for the production of blast-furnace cement were constructed in the Don Basin, Transcaucasus, central regions of the USSR in the Urals, and in West Siberia. The blast-furnace-cement production comprised as much as 35.3 percent of the total amount of the cement output during 1959.

In the USSR along with the construction of large up-to-date equipped plants for making blast-furnace-slag cement, deep theoretical investigations have been conducted. These were devoted to the study of the properties specific to metallurgical slags, to the means of their processing, and to the use of blast-furnace cement in the building industry. Blast-furnace cement has been used in the construction of dams at Dniepr, Kahovka, and other hydro-power stations as well as for many other very important construction projects.

Almost all kinds of slags derived from cast iron, Bessemer, and Martin processing are used to make blast-furnace cement in the USSR.

Nearly 95 percent of all the liquid blast-furnace slags used in the USSR undergo granulation. Granulated slags are used to make cement, mainly blast-furnace cement. They are also used as small additives (up to 15 percent) in making portland cement and as a raw component of clinker. Blast-furnace slags are widely used in the building industry for making grouts and concretes, and are processed for making of thermosit, slag wool, and some other building materials.

Various processing plants are employed to granulate slags. Depending on the moisture content in the granulated slag, these plants are classed as wet or semidry.

Although most of the granulated slag is made in wet granulated plants, its use is less economic as compared with slag from the semidry plants, since the transportation of the latter—especially in winter—and its processing are much less expensive. That is why new wet-granulation plants are not constructed any more, and the old ones are being converted to the semidry process wherever it is possible.

Central granulation plants which are mainly used in the USSR are very effective, and their production capacity amounts to as much as 200,000 to 800,000 tons a year.

They are located near blast-furnace departments and receive liquid slag from a number of furnaces in special slag-conveying buckets. Most of these central plants are destined for wet granulation and are of the granular basin type. There are only two or three steel works served by grout plants.

The drum method for semidry granulation of slags worked out in the USSR is widely used in this country [1].[1]

The principle of action of the drum plant is based on two successive stages of quenching of the liquid slag. During the first stage the melt is quenched with a small amount of water under high pressure, resulting in the foaming of the melt. The foaming depends on the temperature, chemical composition of the slag, and the amount of water supplied.

During the second stage, foamed but still hot and fluid slag is transported to the turning drum where it is quenched by mechanical breaking of its bulk into separate particles and ejecting them into the air. Fast movement of particles in the air helps their quenching and evaporation of the residual entrained moisture.

When using the semidry method of granulation, less decomposition of sulfides and less liberation of hydrogen sulfide take place.

The semidry granulated slag is of a more compact structure; its bulk density is some 1.5 times that of wet granulated slag of the same liquid melt.

The moisture content of wet-granulated slag amounts to 35 percent while that of semidry is up to 10 percent; the bulk density of these granulated slags is 400–1,000 and 600–1,300 kg/m^3 respectively.

According to the data obtained from the study conducted by "Niitsement" [21] the hydraulic properties of semidry and wet-granulated slags of the same chemical composition are practically equal. The chemical composition and hydraulic properties of slags processed by cement and construction industries of the USSR are of great variety. The slags derived from iron works of the south and those of the eastern regions of the USSR differ in both their chemical composition and hydraulicity.

Blast-furnace slags from the southern iron works have low alumina content (6 to 10 percent) and a comparatively high content of sulfide (up to 3 percent). On the other hand slags from the Uralo-Kuznetsk basin, using ores rich in alumina and low-sulfur coke, contain much alumina and little sulfide sulfur (up to 1 percent).

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[1] Figures in brackets indicate the literature references at the end of this paper.

Research work conducted by Soviet scientists shows that, along with lime, alumina is one of the most important active components of granulated slag, which, other conditions being equal, insures high quality of the blast-furnace cement. That is why the evaluation, by its basicity, of any slag to be used for the production of cement has been abandoned in the USSR.

During the thirties it was recognized that the so-called acid granulated blast-furnace slags characterized by percent content of $\frac{CaO+MgO}{SiO_2+Al_2O_3}<1$ are also quite usable for making blast-furnace cement.

The correctness of this assertion was afterwards proved by the wide use of these slags in this country and in some others as well. In recent years, new formulas have been developed in which the content of alumina in slag is considered as a positive factor in the hydraulic properties of granulated blast furnace slag.

Blondiau [5] considers that in slags with sufficient hydraulicity the CaO/SiO_2 ratio should be of the order of 1.45 to 1.54, while the SiO_2/Al_2O_3 ratio should be 1.8 to 1.9.

But all these formulas apparently do not reflect the full relationship existing between the chemical composition of a slag and its hydraulicity.

Stutterheim [6] investigated a great number of slags with the aim of determining their chemical composition and strength at the ages of 28 and 91 days. He defined the hydraulicity of slags by the following series of formulas:

1. $\frac{CaO+MgO+Al_2O_3}{SiO_2}\geq 1$

2. $\frac{CaO+MgO+1/3Al_2O_3}{SiO_2+2/3Al_2O_3}\geq 1$

3. $\frac{CaO+CaS+1/2MgO+Al_2O_3}{SiO_2+MnO}>1.5$

4. $20+CaO+Al_2O_3+1/2MgO-2SiO>12$

5. $S=0.38G(M-0.72)+75$

where:

S=percentage strength of portland cement concrete at the age of 91 days,
G=content of the vitreous phase in granulate,
M=modulus defined by formula 1.

Stutterheim did not find any clearcut relationship between the features studied, indicating that the available formulas fail to reflect distinctly this relationship, which apparently, is considerably more complex.

Nevertheless some of the formulas make it possible to determine approximately the nature of slag.

P. P. Budnikov [7] in the USSR proposed a formula which characterizes the quality of slag by means of the quality factor Q:

$$Q=\frac{CaO+MgO+Al_2O_3}{SiO_2+MnO}>1.$$

One can mention the recent German specification which permits the use of acid slags containing appreciable amounts of alumina for the production of cement.

On the basis of the above, criteria of hydraulicity apparently lie in chemical composition, and the last formulas take into account even the content of manganese protoxide which is known to exercise negative influence on the hydraulicity of slag.

Investigation conducted in the "Niitsement" [8] showed that the low hydraulicity of slags obtained from the production of Martin cast iron, often coupled with an increased manganese content, is the consequence of their low basicity aggravated by the lack of alumina and of the comparatively cold operation of the blast furnace, rather than of the harmful effect exercised by their manganese content.

Slags formed during hot operation of the blast furnace and with an increased content of alumina, even slags with high content of manganese protoxide—e.g., slags of ferromanganese and specular cast irons—have a marked hydraulicity and may be considered suitable for making blast-furnace cement. This was proved by the studies conducted by a number of other investigators [9,10].

Studies conducted in the USSR and in some other countries [6,11] showed that manganese blast-furnace slags have sufficient hydraulicity.

The problems of the structure of the granulated blast-furnace slags are more or less broadly elucidated in special literature. It is proved that increased hydraulicity of quenched slags is the result of converting the structure into a vitreous one—with considerably greater storage of internal energy than is the case with slowly cooled crystallized slags.

A comparison of the heat of dissolving of granulated and slowly cooled slags of the same chemical composition proved what has been said before—i.e., granulated slags liberated more heat.

Microscopic study of basic granulated blast-furnace slags of high hydraulicity showed, however, that the amount of vitreous phase in these slags is comparatively limited, of the order of 15 to 45 percent. But acid granulated blast-furnace slags, vitrified during the granulation process to 80 percent and more, do not have hydraulicity comparable to basic slags. The hydraulicity of acid slags obtained from the charcoal cast-iron process is very low despite their complete vitrification.

In acid slags, along with the crystallization of the minerals of the melilite group, there often appears calcium silicate—$CaO \cdot SiO_2$—in the form of pseudowollastonite.

The crystallization of this mineral is specific for acid slags with relatively low alumina content. In the case of an increased content of alumina, predominance of the formation of anorthite—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—is observed. The precipitation of calcium and manganese sulfides sometimes is also observed in acid granulated slags.

Studies conducted in our country [13] demonstrate that not all of the sulfide sulfur which is present in slags is combined in CaS. At first the sulfur combines with manganese and iron, and only after that does it combine with calcium. The calculation of the CaS content in blast-furnace slag should be made with due consideration of this fact.

Therefore the hydraulicity of slags is a function not only of high content of the vitreous phase but also of the chemical composition of this phase and of the crystalline formations.

Nowadays there is not any universally adopted theory on the hardening of slag cements. The roles of the mineralogical components and of the vitreous phase in this process are not yet completely clear.

It is supposed that under the influence of alkali hydroxide, colloidization of the surface layers of the vitreous grains takes place, since these grains are a less-stable phase due to the quenching of the granulation process; during this reaction, silica gel precipitates which partly reacts with lime and cements the grains of the slag into a solid monolithic body.

The process of hardening of blast-furnace slags is explained by some as a result of the formation of hydrated silicates and aluminates of calcium. This process is very slow but can be markedly accelerated under the influence of acid and sulfate stimulants.

Recently a theory of electrolytic activation of blast-furnace slags is attracting more and more attention. This theory is as follows. In melted blast-furnace slags a considerable part of the chemical compounds is in a state of dissociation. During the quenching there is no time for stable chemical compounds to form, and the melt has therefore a considerable amount of Ca, Mg, AlO_4 and SiO_4 ions. During hydration, water acts on these unstable dissociated groups; the slag glass is destroyed, and the ions are again able to be mobile in aqueous media. Under the influence of activators, neutralization of oppositely charged ions and crystallization of newly formed hydrated products take place.

Soviet scientists [13, 16, 19] investigated the problems of studying the features of sulfate and acid stimulation of slags; they studied new formations appearing in hydrating slag and slag binders.

The treatment of slags of different composition with water, gypsum water, lime water, and with the mixture of the last two show that the greatest effect is obtained when using lime—pure or with an addition of material having a common ion with lime (leaches, $CaCl_2$). The action of the last, without lime, is considerably weaker, and it is found that hydroxyl ion gives rise to more intensive hydration of slags than Ca ion ($CaCl_2$). It is possible that exchange reaction between leach and slag takes place in the first case, that is to say, that some lime is formed.

Gypsum also stimulates the hydration of slags through adsorption, forming poorly soluble complex salts with aluminates, etc.

Sulfates however, need a kind of a "mediator"—lime—and without it have no importance of their own.

It is found that if portland cement is used for an activator of a slag, then a small addition of it brings a sharp change in the qualities of the binder, with approximation to the more active component, i.e., to cement.

The investigation of new formations appearing during the interaction of the slag and the water shows that these new formations contain the same chemical constituents as the starting slag but in other proportions [19, 20, 21]. The nuclei of the new formations consist of the smallest particles of slag but not of its components. It is found as well that the basicity of the new formations is higher than that of the starting slag, that alumina characteristics develop, which indicate the active role of aluminates and, finally, that the new formation combines water vigorously.

In order to determine the hydraulic properties of the separate minerals of a slag, the "Niitsement" has conducted some studies [16]. These studies show that without activating agents neither mineral gehlenite nor gehlenite glass harden whether they are subjected to ordinary temperature, common steam curing, or high-pressure steam curing. These studies show that when gehlenite glass is mixed with lime water, hexagonal plates of calcium hydroaluminate appear; when some gypsum is added to this mixture, there occurs formation of needles of calcium hydrosulfoaluminate. Mineral akermanite hardens without adding activators only under high-pressure curing; akermanite glass hardens at ordinary temperature, but more intensively under steam curing—common and high-pressure as well. Crystalline anorthite and anorthite glass have no hydraulic properties.

High-alumina blast-furnace slags used in making alumina cement are characterized by different properties. For example, crystallized slags have higher strength when hardening than vitrified ones. Generally it can be stated that the minerals which, in their crystalline state, have obvious hydraulicity and are liable to independent hardening—e.g., calcium aluminates and silicates—lose this property in their vitreous state.

So, one can see that the hydraulicity of a blast-furnace slag obtained when processing either common cast iron or that destined for steel making depends on a combination of a great number of factors. These include: the temperature of the slag tapped off the blast furnace, its chemical composition, the character and the speed of granulation, and the resulting mineralogical composition of the slag.

The formulas derived from the chemical composition of a slag coupled with crystallo-optical data can give but an approximate indication of its hydraulicity. The degree of suitability of a particular quenched blast-furnace slag for cement manufacture should be determined mainly on the basis of study of test specimens of blast-furnace cement, the clinker of which is mixed with various portions of the slag, and which is ground to the specific surface common for this plant. There are some other practical methods to determine the hydraulicity of granulated slag, e.g., laboratory tests of specially combined mixtures of clinker, slag, and quartz sand [3], and measurement of the amount of gypsum absorbed when the slag powder is boiled in a lime-gypsum solution.

The last method has practical meaning as well for determination of the optimum content of gypsum when making blast-furnace slag cements of the highest strength. Besides these methods, there are some others.

In common practice of cement manufacture, clinker, dried granulated slag, and gypsum are ground together to the fineness (specific surface) desired.

Until recently it was supposed that the lowered output of compartment tube mills when grinding blast-furnace cement was a function of lower grindability of the slag. However, recent study by the "Niitsement" showed that basic wet-granulated blast-furnace slags, yielded when processing cast and steel-making iron, are ground relatively faster than clinker and are present in cement mainly in its finest fraction. The reduction of the mill output should be explained as a function of the low specific volume of slag which limits the possibility of filling up the mill sufficiently.

When using acid blast-furnace slags of wet—and especially semidry—granulation, other results are obtained. During ordinary grinding of clinker with these slags, they do not concentrate in the finest fraction of the cement powder, despite their considerable glass content.

High fineness of grinding—an increased specific surface—is especially necessary to display the potential physico-chemical activity of a slag; and it is natural that the less active the slag, the finer it should be ground.

This requirement should be taken into consideration when qualifying granulated blast-furnace slag as an active hydraulic component of blast-furnace cement.

Long experience in the production and application of blast-furnace cement has revealed a number of very important construction properties.

Wide scientific and experimental investigations devoted to the study and improvement of the properties of blast-furnace slag cement are being conducted in the USSR.

Blast-furnace cement is a complex binding agent. Its properties depend on a great number of factors the combination of which makes a complicated system of interaction.

The brilliant feature of blast-furnace slag cement is the comparatively high value of its tensile strength which results in a low ratio of compressive strength to tensile strength.

As distinct from pozzolanic cements, blast-furnace cement does not require increased water consumption when used for grouts and concrete mixtures. Though there is rather delayed attainment of strength during the first period after mixing, this cement is distinguished by intense attainment of strength at later ages.

It can be said, generally, that the strength of portland cement between 1 and 7 days may approximately double, while that of blast-furnace cement may triple, under normal conditions of temperature and moisture.

The slower hardening of blast-furnace cement causes less heat liberation during the hydration, which is very important for the use of this cement in mass concrete.

Low water permeability and the higher corrosion resistance of blast-furnace cement in mineralized water make possible its use in hydraulic structures. Besides this, blast-furnace cement undergoes less contraction and has higher frost resistance in comparison with pozzolanic portland cements. But its most important property in comparison with pozzolanic cement is its relative stability in air, and this property provides normal hardening of concrete and reinforced concrete in land structures. Of course it does not exclude the necessity of carefully curing the concrete to protect it from drying and from low temperature during its first period of hardening.

Steam curing used in manufacture of concrete and reinforced-concrete articles is especially favorable for blast-furnace cement.

These are all reasons to consider blast-furnace slag cement a more universal binding agent than pozzolanic cement, and therefore it can be used for submarine, underground, and land structures and, practically, its most valuable properties can be used for the first two types of constructions mentioned.

The "Niitsement" has conducted studies of the properties of blast-furnace cement for using it in hydraulic structures [23].

The study of contraction and the combining of water during the hydration of blast-furnace cement reveals that the addition of slag lowers the contraction and that during the first day this lowering is proportional to slag content in the cement.

In the case of equal ratio of the slag and clinker, more contraction to the age of 30 days is observed in blast-furnace slag cement containing basic slags. The contraction of the blast-furnace slag cement with acid slags depends mainly on the chemical-mineralogical composition and the specific surface of the clinker component.

The amount of water combined by cements during the hydration depends mainly on the activity of their clinker component. To the age of 3 months, blast-furnace cements of various compositions combine some 10 to 12 percent of water relative to the weight of cement. In the case of blast-furnace cements with acid slags this amount of water binds mainly their clinker component, which, when different cements are ground to equal specific surface, is subjected to finer grinding in blast-furnace cements than in portland cement and therefore hydrates quicker. Quicker hydration of blast-furnace cement is a result of the fact that the particles of the slag move apart the grains of clinker and facilitate the access of water.

The heat liberation of blast-furnace slag cement appreciably depends on the exothermic effect taking place during the hydration process of the clinker component since acid slags in the course of 3 days hydrate only as much as 5 to 6 percent. It is quite natural, that with increase of clinker content in a blast-furnace cement its heat liberation increases as well.

The presence of a slag in cement lowers its heat liberation disproportionately to the amount of the slag added.

Acid or basic slag added to a portland cement in an amount of 50 to 70 percent decreases the heat of its hydration to the age of 3 days up to 30 to 58 percent.

The study of the phenomenon of contraction of blast-furnace cement has revealed that basic slags decrease the contraction of cement due to good adhesion of particles of the slag with hydrated grains of clinker, greater compactness of the cement paste, and less loss of water.

The reason for the contraction of blast-furnace cements in air hardening lies mainly in the removal of uncombined water; in the case of blast-furnace cements with small addition of slag—less than 50 percent—the contraction to some extent depends on the mineralogical composition of the clinker as well. Contraction strains in the case of a grout of blast-furnace cement with normal sand, of 1:3 ratio, at the age of 4 months of air hardening amount to 0.6 to 0.76 millimeters per meter with either 50 percent of acid or 70 percent of basic blast-furnace slag in the cement; contraction of pozzolanic cement taken for comparison amounted to 1.15 millimeters per meter.

Investigation of the resistance of blast-furnace cements containing acid or basic slags to the effect of leaching by distilled water shows that the addition of acid or basic slags to cements increases their durability to the effect of soft water, and this increase is characterized by decrease of the absolute amount of lime leached out of blast-furnace cement and by decreased loss of strength as compared with portland cement and pozzolanic portland cement.

Solid grains of a slag which hydrate rather slowly make a kind of additional rigid structure, and this, after the leaching of some part of the lime from the clinker constituent of the cement, suffers no change.

Blast-furnace cements have sufficient frost resistance which can be increased by adding some surface-active agents, decreasing the water-cement ratio, and by preliminary hardening for approximately 3 months before the frost exposure starts. Securing of these last conditions is especially important for blast-furnace cement made with acid slags which, containing more "weakly combined" water, are therefore less frost resistant than blast-furnace cements made with basic slags.

As to the water resistance of blast-furnace cement, the type and the degree of dispersion (specific surface) of the slag used are of essential importance.

Low water permeability of concretes made with blast-furnace cement can be attained by empirical determination of the necessary fineness of grind of the components of the cement.

Since fine grinding has a beneficial effect on the most important building properties of blast-furnace cement, its manufacture for hydraulic structures through separate grinding of slag and clinker should be considered rational. Wet grinding of slag, which considerably facilitates the making of fine fractions, also gives good results.

Nevertheless the retarded rate of strength attainment during the first period of hardening led to the endeavor to accelerate the rate of hardening of blast-furnace cement. Conditions for making high-grade blast-furnace cement on the basis of common granulated blast-furnace slags, of cast and steel-making iron, were studied in the "Niitsement" [24]. The results obtained show that for blast-furnace slag, and for portland cement as well, the chemical-mineralogical composition of the starting clinker has considerable importance. In this case, particularly, higher content of the clinker minerals most active at the earlier ages, C_3S and C_3A, is required.

Increase of the specific surface of blast-furnace cement, resulting in considerable activation of slag and clinker, is an effective means of accelerating the hardening.

Increase of the specific surface of the blast-furnace cement to 1.5 to 2.0 times (up to 4,000 to 4,500 cm^2/g, Blaine) helps to increase its strength to that of the starting portland cement with specific surface of 2,500 to 3,000 cm^2/g.

Investigation of the properties of blast-furnace cement made by fine and superfine grinding in the "Niitsement" [25] shows that it is possible to make blast-furnace-slag cement of high strength by means of finest grinding—even on the basis of weakly active granulated slags. The chemical composition of a slag has an essential influence on the activity of a superfine blast-furnace cement, but only during its early ages of hardening.

The strength of superfine blast-furnace cement at 28 days is 100 to 200 percent more than that of the same cement of usual fineness. However, sharp attainment of strength resulting from the superfine grinding of blast-furnace cement, is displayed at early ages of hardening.

Superfine grinding of blast-furnace cements made from weakly active acid and low basic slags is especially effective.

Superfine grinding makes possible wide use of weakly active slags in the cement industry.

One of the main methods of finer grinding of blast-furnace cement should be the separate grinding of slag and clinker which permits one to regulate and to pre-establish the most effective specific surface of every component.

This method should be especially necessary for blast-furnace cements made with acid slags inasmuch as acid blast-furnace slags, to reveal their potential hydraulicity, need finer grinding than basic slags.

Studies conducted in the "Niitsement" and in the "Yuzhgiprotsement" [26] show that high-early-strength blast-furnace cement with compressive strength at ages of 1 and 3 days like that of high-early-strength portland cement can be made with 30 to 40 percent of granulated blast-furnace slag, using active clinker and fine cement of common or separate grinding to approximately 4,500 to 5,000 cm^2/g, Blaine.

The production of high-early-strength blast-furnace cement is organized now on a commercial scale.

Introduction of 30 to 40 percent of basic blast-furnace slags into magnesia portland cement, having up to 10 percent of MgO, and made in our country in small quantity, is very effective.

Slag magnesia portland cement as well as blast-furnace cement is distinguished from portland cement by somewhat more retarded hardening and by lower strength.

Slag magnesia portland cement is used in our country for various types of construction.

The use of blast-furnace slags for the manufacture of melted cements is of great interest.

A method of slag processing to make melted cements was invented by V. V. Serov, a Soviet inventor, and this method is introduced in practice in the Soviet Union [27].

Up to the present there has been known only one secure method of making melted cement clinker by means of concentration of liquid slags outside of the blast-furnace. This method was offered by K. Wennerström, a Swedish engineer [28]. By this method, liquid slag is concentrated in an electric furnace lined with carbon and equipped with graphite electrodes. However, this method can be used on a commercial scale only when cheap power is available since its power consumption, according to the data of the inventor, amounts to 400 to 700 kwh per ton of clinker.

Besides this disadvantage, as a result of the contact between the carbon of the lining and the lime, an appreciable amount of calcium carbide forms. This, dissolving in the clinker, changes it for the worse.

From the very beginning, the experimental working out of Serov's converter was aimed at solving the most difficult task: to make melted portland cement clinker from liquid blast-furnace slags.

An important feature of the design of this converter is the absence of a refractory lining for which is substituted a layer of slag hardening on the surfaces of the steel caissons and cast-iron cooling plates which make up the walls and the dome of the converter. These caissons and plates are vigorously cooled by water (fig. 1). The converter is fired by mazut.

Air coming to the tuyeres of the converter is heated by the exit waste gas, for which purpose two hot-blast stoves serve. These resemble blast-furnace stoves. In order to reach the high temperature necessary, the air in the converter is, after this heating, supplied with additional oxygen.

The making of melted portland-cement clinker by concentrating liquid blast-furnace slag is as follows. As the temperature of the melt rises, lime (either limestone, or burned lime) is added to liquid slag poured from a slag bucket into the converter, approximately to the level of 1 meter above the material-and-fuel injecting pipe; to lower the temperature of melting of the product, iron oxide in the form of iron ore is added. The lime and the ore are ground to the size of 10 to 40 mm before being conveyed to the converter.

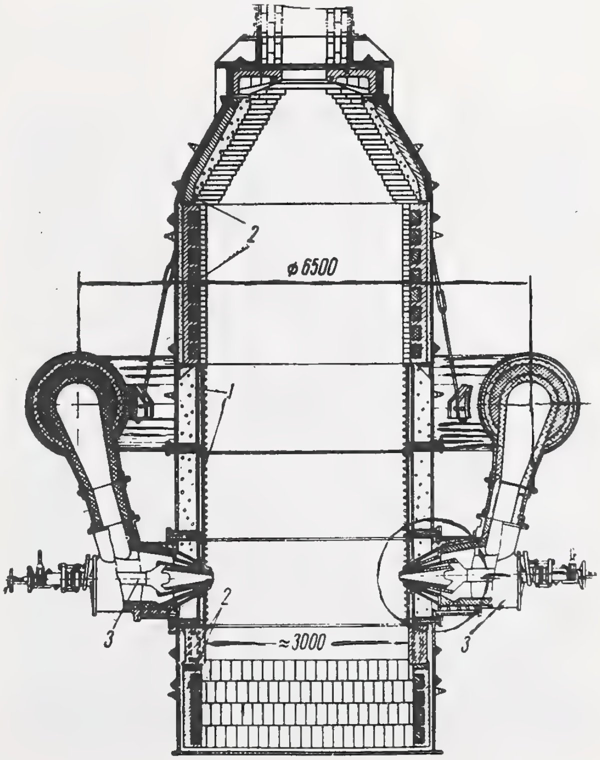

Figure 1. *Sectional drawing of the converter.*

1—steel caissons; 2—cast-iron cooling plates; 3—injection pipe for material and fuel.

The finished clinker melt is let out of the converter and subjected to granulation. With the aim of comparative investigation of the properties of the melt, it was either granulated or cooled in a layer.

Investigation of melted clinker reveals that granular clinkers are characterized by a very fine-granular and original structure of the minerals, which is not characteristic of the clinkers made by sintering. Alite has the form of very elongated prisms, which are sometimes almost acicular, with dimensions

$5 \times 25\mu$ to $5 \times 125\mu$.

There are groups of the finest grains of belite and the ferrous phase between the prisms (figs. 2 and 3).

The appearance of slowly cooled clinker, the specific feature of which was an extremely macrocrystalline mineral structure, was of a radically different nature.

The sizes of the crystals amounted to 400 to 500 μ. In some pieces of certain fusions the crystals of alite could be seen with the unaided eye.

Alite had the form of hexagonal plates with clearly shaped cleavage cracks and with a lot of defects in the form of air bubbles and ferrous inclusions.

The character of crystallization of belite also varied, depending on quenching.

In granulated clinkers belite either had the form of very fine rounded grains aggregating with one another and closely intergrown with ferrous phase or was in dendrite formations (fig. 4).

In slowly cooled clinkers we observed belite as shapeless formations and coarse rounded grains with highly perfect cleavages and granular surfaces.

High-grade melted portland-cement clinker was made with the following parameters of the process of melting:

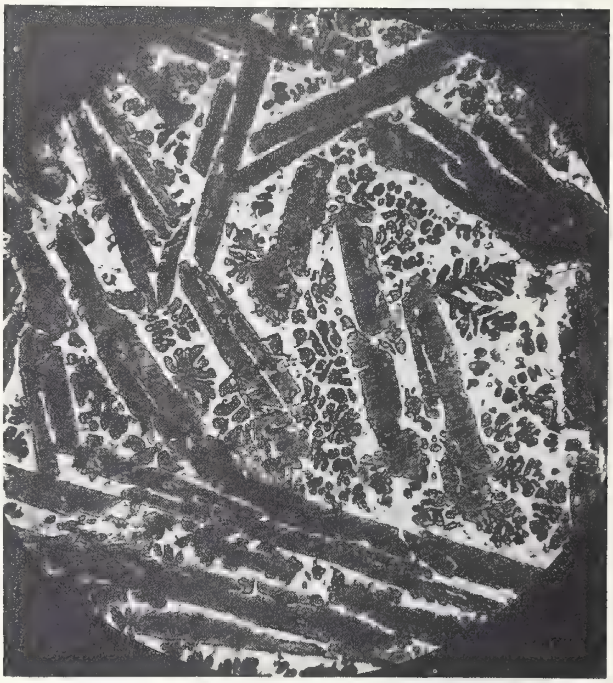

FIGURE 3. *Microstructure of granulated clinker.*
Reflected light. Magnification ×440.

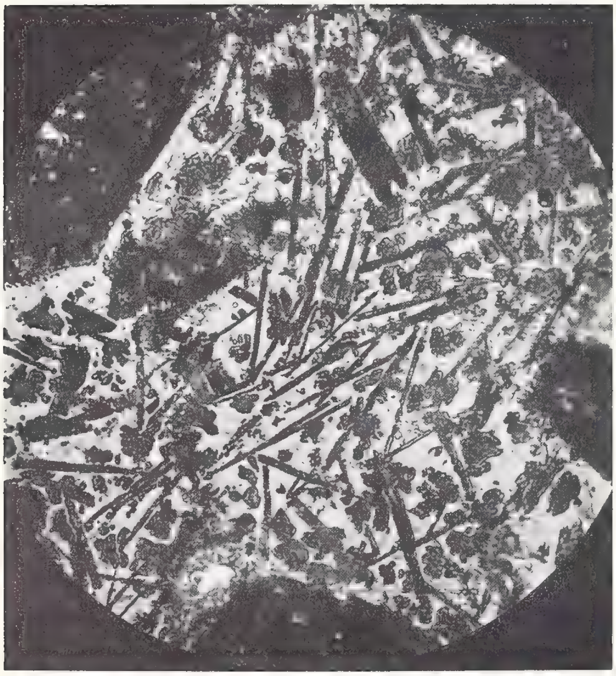

FIGURE 2. *Microstructure of granulated clinker.*
Reflected light. Magnification ×440.

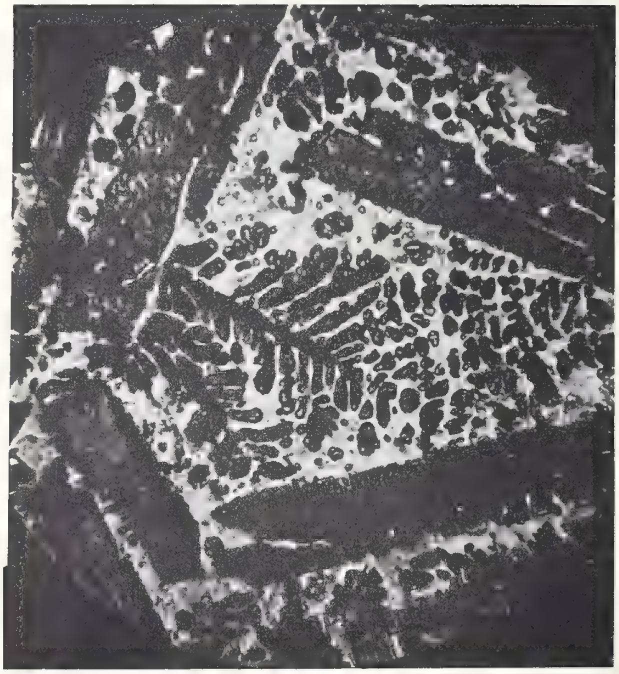

FIGURE 4. *Microstructure of belite in granulated clinker.*
Reflected light. Magnification ×440.

CaO cement in blast-furnace slag charged to converter, percent	46–48
Temperature of the slag charged, °C	1, 300–1, 350
CaO content of the clinker melt discharged from converter, percent	60–63
Temperature of the clinker melt being discharged, °C	1, 900–2, 000
O_2 concentration in air, percent	26–28
Temperature of blowing, °C	700–800

The problem of using slags for the purposes of cement technology is being progressively solved by investigations. Great and important tasks are on the way to completion.

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Paper VIII-S4. High Chemical Resistance Pozzolanic Cements*

R. Turriziani and A. Rio

Synopsis

The influence of the reactive silica occurring in pozzolanic materials on the chemical resistance of pozzolanic cements from a general viewpoint and, particularly, towards selenitic water is pointed out by the authors.

The reactive silica seems to diminish the possibility of new formation of calcium aluminates and to fix preferably the hydrolysis lime of clinker. Furthermore, the gels of hydrated calcium silicate resulting from the reaction between silica and hydrolysis lime would have an efficacious protective action for the aluminates already present which are thus preserved from coming in contact with aggressive solutions.

Therefore, it is possible to graduate the chemical resistance of the pozzolanic cements to make them resistant even to the severe conditions of the Anstett test by modifying the reactive silica/reactive alumina ratio. This result is reached at a value of about 6.

Résumé

Les auteurs mettent en évidence l'influence que la silice réactive présente dans les matériaux pouzzolaniques manifeste sur la résistance chimique en général, en particulier aux eaux séléniteuses, des ciments confectionnés avec eux.

Il résulterait qu'une telle silice réactive diminue la possibilité de néo formation des aluminates de calcium, en fixant de préférence la chaux d'hydrolyse du clinker. Les gels de silicate de calcium hydraté produits par la réaction de la silice avec la chaux d'hydrolyse auraient en autre une action protectrice efficace sur les aluminates présentes en les préservant du contact des solutions aggressives.

Il est possible cependant de graduer, en modifiant le rapport entre la silice et l'alumine réactive présentes, la résistance chimique d'un ciment pouzzolanique jusqu'à le rendre résistant aux sévères conditions de l'essai Anstett. Ce résultat s'obtient avec une valeur du rapport d'environ 6.

Zusammenfassung

Die Verfasser heben den Einfluss der in puzzolanischen Stoffen anwesenden reaktiven Kieselsäure auf die Widerstandsfähigkeit gegen chemische Angriffe im allgemeinen hervor, und besonders gegen den Angriff der Sulfatwasser.

Reaktive Kieselsäure scheint die Möglichkeit der Neubildung von Kalziumaluminate zu vermindern, indem sie vorzüglich den Hydrolysekalk des Klinkers bindet. Die Gele des aus der Reaktion der Kieselsäure mit Kalk entstehenden hydratisierten Kalziumsilikates üben eine Schutzwirkung auf die anwesenden Aluminate aus, indem sie die letzte vor der Berührung mit aggressiven Lösungen bewahrt.

Es ist deshalb möglich, die chemische Widerstandsfähigkeit eines puzzolanischen Zementes so zu graduiren, indem das Verhältnis zwischen der anwesenden, aktiven Kieselsäure und Tonerde modifiziert ist, dass das Zement besteht sogar die strengen Bedingungen der Anstett- Probe. Dieses Ergebnis wird mit einem Werte von etwa 6 erreicht.

Introduction

In relation to the paper on the constitution and properties of pozzolanic cements by G. Malquori, we think it would be useful to make a more careful investigation of a certain characteristic aspect of the chemical resistance of the binders in question, that is the influence of reactive silica contained in pozzolanic materials on their usual chemical resistance from a general standpoint and particularly towards sulfate-bearing waters.

The present knowledge of the chemistry of hydraulic binders does not allow us to bring the differences found or supposed among the phases of hydrated pastes of portland or pozzolanic cements into relation with their different chemical resistance.

In this connection the investigators agree that, from a qualitative viewpoint, there are not sufficiently marked differences to account for the different behavior of the two binders in practice. Therefore, the undoubtedly better chemical resistance of pozzolanic cements would depend on a different phase distribution in the hydrated pastes.

To explain this difference, the indirect way seemed to be the more convenient, because of the availability of natural pozzolanic materials of very different compositions (some of them contain almost exclusively reactive silica).

We started, therefore, from the assumption that the different behavior of the two types of binders must be due to the different amount of hydrated calcium silicate gels in the pastes.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Rome and Centro Studi della Società Cementisegni, Rome, Italy. (This paper was presented at the Symposium by A. R. Collins.)

It is not our purpose, at present, to investigate the possibility of a differentiation between structure and composition of the gels formed in both cases, although this side of the question would play an important role in the matter. At any rate we may foresee that the gels would effect a remarkable protective action on the phases more susceptible to attack, since by their nature they hinder the ion diffusion and exchange reactions between the hydrated products of the pastes and the contact solutions.

Experimental Investigation

The compositions of the materials used in our test are given in table 1. They are: a portland clinker with low iron modulus, a normal portland clinker, and two natural pozzolanic materials with different reactive-silica content. We indicated by P_1 a pozzolana with a high reactive-silica content and by P_2 a pozzolana whose content in reactive silica corresponds to that of the usual latial pozzolanas.

Table 1. *Composition of two clinkers and two pozzolanic materials*

Chemical analysis

	Normal portland clinker	Low-iron-modulus clinker	Pozzolana P_1	Pozzolana P_2
Ignition loss, %	1.60	0.60	4.80	5.63
SiO_2, %	21.00	21.45	88.25	44.92
Fe_2O_3, %	2.76	4.54	.32	9.70
Al_2O_3, %	6.34	3.96	1.80	17.58
CaO, %	66.50	66.20	1.68	11.02
MgO, %	1.00	1.20		
SO_3, %	.80	.63		
M.I.[a]	2.21	2.21		
M.S.[b]	2.30	2.52		
M.F.[c]	2.29	.87		
C_2S, %	51.58	64.00		
C_3S, %	21.32	13.00		
C_3A, %	12.13	3.00		
C_4AF, %	8.40	14.00		
Lime saturation, %	97.6	98.0		
Malquori residue, %	-----	-----	4.00	13.10

[a] Hydraulic modulus.
[b] Silica modulus.
[c] Iron modulus.

Progressive solubilization of SiO_2 and R_2O_3 according to Florentin, given as % total SiO_2 and R_2O_3

	Pozzolana P_1		Pozzolana P_2	
	SiO_2	R_2O_3	SiO_2	R_2O_3
Initial	5.84	32.04	6.67	44.71
After 3 days	8.87	32.52	11.02	45.99
After 7 days	30.48	41.26	19.44	54.20
After 28 days	52.96	62.62	29.02	66.37

Two series of cements were prepared with the two clinkers; that of the low-iron-modulus clinker is indicated by capital letters and that of the clinker with higher iron modulus by numbers. Each of them includes binary and ternary cements. The former were prepared by mixing clinker with one of the two pozzolanas, the latter by adding different amounts of both pozzolana P_1 and pozzolana P_2. The weight ratios of materials constituting each pozzolanic cement are shown in table 2.

Table 2. *Percentage of the materials composing the two series of cements*

Sample		Clinker	Pozzolana P_1	Pozzolana P_2
Series 1–10 normal portland clinker	Series A–L low-iron-modulus clinker			
1	A	100	-----	-----
2	B	65	-----	35
3	C	65	5	30
4	D	65	10	25
5	E	65	15	20
6	F	65	20	15
7	G	65	25	10
8	H	65	30	5
9	I	90	10	-----
10	L	80	20	-----

The whole pozzolanic addition was limited to a maximum of 35 percent, which value corresponds to the average pozzolana content of commercial pozzolanic cements. In this way two series of cements with different content in reactive silica and alumina were obtained.

The petrographic investigation shows that pozzolana P_1 is constituted by an amorphous or cryptocrystalline groundmass including a number of crystals at a different stage of alteration. The crystalline phases are feldspars and, less frequently, biotite, quartz, calcite, and zeolites; fragments of diatoms were also observed.

As may be inferred from the chemical constitution (low content of alumina, ferric oxide, calcium oxide, and carbon dioxide) and from the negligible residue after Malquori base-acid attack [1][1], the content in crystalline phases is very low. This is also confirmed by the X-ray pattern of this material which does not present a system of lines, but shows a band at 4.05 A (fig. 1), similar to the dried silica gels.

The infrared spectrum (fig. 2) was obtained with a double-beam Leitz apparatus. The sample was ground very fine, mixed with potassium bromide in a weight ratio of 1/10 and made up into tablets. The spectrum presents characteristic bands at 9.5–9.6μ, 10.6–10.8μ, and 12.5–12.6μ, respectively. The highest intensity is shown by the first band, which is very wide and irregularly defined. This band and the third one are characteristic of all types of silica, while the second band is probably due to SiOH groups. The position, form, and amplitude of the bands indicate that the material consists of silica gel. Similarly to silica gel, the material P_1 reacts quickly with calcium hydroxide forming a calcium silicate of the

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[1] Figures in brackets indicate the literature references at end of this paper.

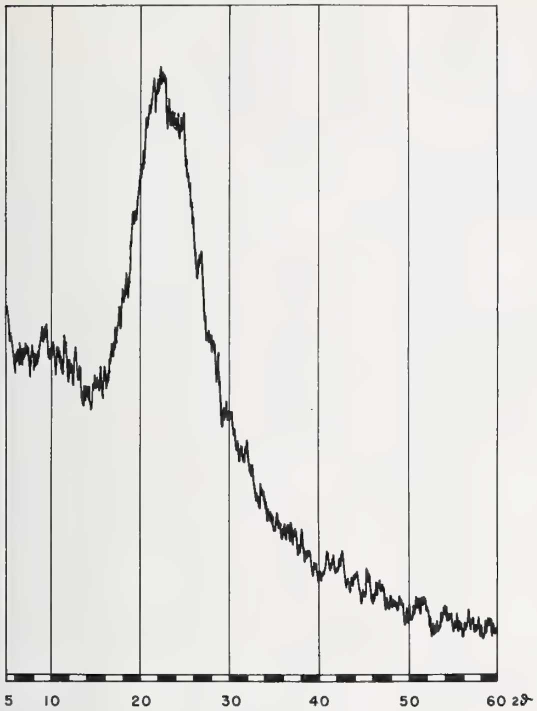

FIGURE 1. *X-ray diffraction pattern of pozzolana* P_1.

tobermoritic type. The reactive silica constitutes more than 90 percent of the total silica.

The silicate formation may be easily followed both by X-ray and by infrared methods. In the former case the phenomenon is revealed by the appearance of the reflection at 3.06 A, practically the only one of the whole spectrum, and by the disappearance of the band at 4.05 A.

In the latter case the presence of silicate is inferred by the position of the most intense band, which is displaced towards greater wavelengths and appears at about 10.2μ for the silicate with a ratio $CaO/SiO_2 > 0.8$ [2]. Launer [3] assumes that this band is characteristic of all silicates containing chains of SiO_2 tetrahedrons.

The pozzolana P_2 is a typical Roman pozzolana. Unlike the other type, this pozzolana fixes calcium hydroxide at a lower rate and in a smaller total amount, and, furthermore, it contains reactive alumina.

According to data in our possession, the maximum amount of lime that can be fixed by pozzolana P_2 is about 50–60 percent. In the case of materials almost saturated in lime, the quantities of silica and alumina rendered soluble by the Florentin acid attack amount to about 65–70 and 70–75 percent respectively, after a curing period of about 2 yr.

Two types of test were used for controlling the chemical resistance of the pozzolanic cements having the compositions shown in table 2. They are as follows:

(1) Test for the long-time behavior of porous mortars cured under water and then immersed in aggressive magnesium sulfate heptahydrate solution.

(2) Resistance to Anstett test. This test consists in checking the expansion, after 90 days, of specimens prepared with hydrated cement pastes, ground, mixed with 50 percent by weight of gypsum, and cured in a humid atmosphere.

While the first method, in spite of the time required, is sufficiently indicative for the evaluation of the chemical resistance of the binder in operation, the Anstett test provides in this sense less reliable results, since the carrying out of the test omits a series of factors, such as mortar compactness and surface condition, which play an important role in the behavior of the manufactured product in contact with aggressive solutions.

Nevertheless, in spite of these omissions, the method was included in our program of work since, because of its particularly severe nature, it would have made it possible to ascertain, in the case of a negative result, the existence of the relationship between the content in reactive silica of pozzolana and the chemical resistance of pozzolanic cement.

The tests with aggressive solution of magnesium sulfate were carried out on 4 x 4 x 16-cm specimens, manufactured with monogranular quartz sand in

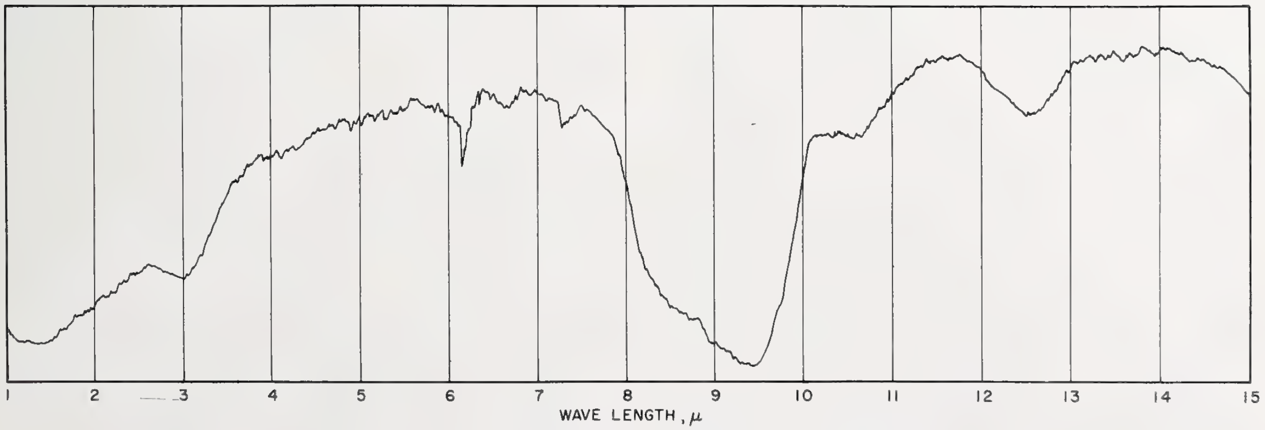

FIGURE 2. *Infrared absorption spectrum of pozzolana* P_1.

order to obtain a high percentage of voids, with a ratio of one part of binder to three parts of sand.

After curing for 28 days in water, they were half immersed in the aggressive solution. In this way two forms of contact were realized: in the lower part by direct imbibition and in the upper part by capillarity. The aggressive liquid consists of a 3 percent solution of $MgSO_4 \cdot 7H_2O$, renewed every week. The specimens remained under observation for 1 yr. The Anstett test was carried out as established by Blondiau [4].

For each paste tested by the Anstett method the diameter of the specimens was measured at 7, 30, and 90 days, and thus the expansion was determined. On the pastes stored for 90 days, besides expansion, the amount of silica and alumina soluble in the Florentin base-acid attack was determined, and the X-ray analysis was also carried out, to check the relationship between expansion and ettringite formation.

It would be considered that, in the case of portland cement pastes, silica and alumina soluble under the conditions of the Florentin attack correspond, in fact, to the content of the two oxides of the clinker. In the case of pozzolanic cements the situation is different: the amounts of soluble silica and alumina increase with the progress of the reaction between calcium hydroxide and pozzolanic material (see table 3).

TABLE 3. *Percentages of* SiO_2 *and* Al_2O_3 *soluble by the Florentin attack, and the* SiO_2/Al_2O_3 *ratio in solution*

(Cured for 3 months)

Sample	SiO_2	Al_2O_3	SiO_2/Al_2O_3
Series 1–10			
1	77.33	22.66	3.41
2	70.77	29.22	2.42
3	74.93	25.06	2.99
4	79.04	20.95	3.77
5	82.29	17.70	4.64
6	85.15	14.84	5.73
7	87.33	12.66	6.89
8	89.09	10.90	8.17
9	81.67	18.32	4.45
10	85.25	14.74	5.78
Series A–L			
A	84.11	15.88	5.29
B	74.50	25.50	2.92
C	78.61	21.38	3.67
D	82.65	17.34	4.76
E	85.79	14.20	6.04
F	87.95	12.04	7.30
G	90.15	9.84	9.16
H	91.98	8.01	11.48
I	87.24	12.75	6.84
L	89.74	10.25	8.75

Discussion of the Results

As was foreseen on the basis of the above-mentioned reservation, the behavior of the two series of cement under study is different according to the method adopted for checking the chemical resistance.

While all pozzolanic cements show generally a good resistance by the method of storage in aggressive solution, confirming the results in practice, they behave differently under the Anstett test, according to their composition.

In particular, all the pozzolanic cements of the series indicated by letters proved resistant to the attack of the aggressive solution. Among the pozzolanic cements of the numbered series, specimen No. 9 showed its first cracks after 6 months, and appeared fissured after 1 yr (table 4). As was to be expected, the specimens manufactured with the two portland cements appeared attacked when the test was over. The specimens prepared with normal portland cements are entirely disintegrated, while those of low-iron-modulus cement show only some cracks. The etching of the latter was very slow, and the first cracks appeared after 90 days, when the specimens of normal portland cement were already split.

In figures 3 and 4 the expansion as percentage of the initial diameter of the specimens is plotted against time for the pastes of series A–L and for those of series 1–10, respectively.

TABLE 4. *Chemical resistance test of pozzolanic cement samples*

Behavior of specimens prepared with porous 1:3 mortar etched with an aggressive solution (3 percent $MgSO_4 \cdot 7H_2O$)—Specimen size 4 x 4 x 16 cm

Sample	Appearance of specimens at different curing times			
	1 month	3 months	6 months	1 yr
Series 1–10				
1	First cracks	Fissured	Disintegrated	Disintegrated.
2	Sound	Sound	Sound	Sound.
3	do	do	do	Do.
4	do	do	do	Do.
5	do	do	do	Do.
6	do	do	do	Do.
7	do	do	do	Do.
8	do	do	do	Do.
9	do	do	First cracks	Fissured.
10	do	do	Sound	Sound.
Series A–L				
A	Sound	First cracks	First cracks	Fissured.
B	do	Sound	Sound	Sound.
C	do	do	do	Do.
D	do	do	do	Do.
E	do	do	do	Do.
F	do	do	do	Do.
G	do	do	do	Do.
H	do	do	do	Do.
I	do	do	do	Do.
L	do	do	do	Do.

Table 3 shows the amounts of soluble silica and alumina for the two series of pastes after 90 days curing, given as percentages of the sum (sol. SiO_2+sol. Al_2O_3) related to the calcined sample, and the ratio of sol. SiO_2/sol. Al_2O_3.

The behavior of the two series of pozzolanic cements under the Anstett test is particularly indicative of the influence of the composition of pozzolanic materials.

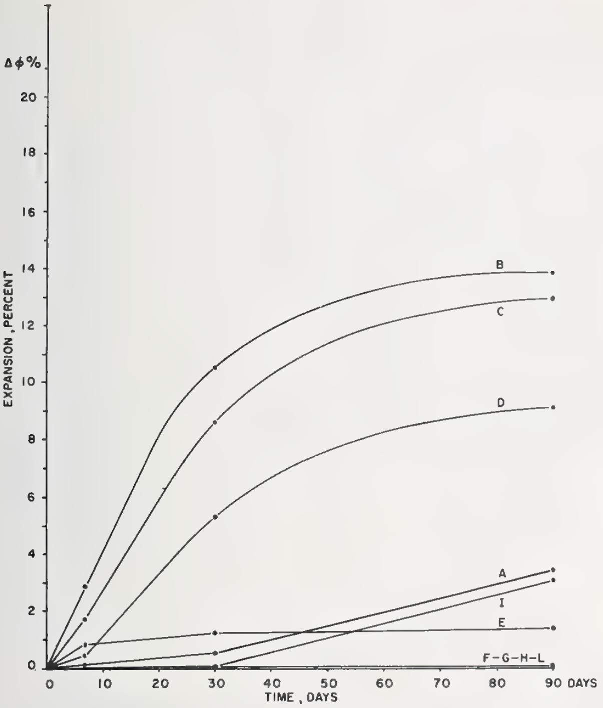

Figure 3. *Expansion of Anstett test specimens.*
Cements: Series A–L

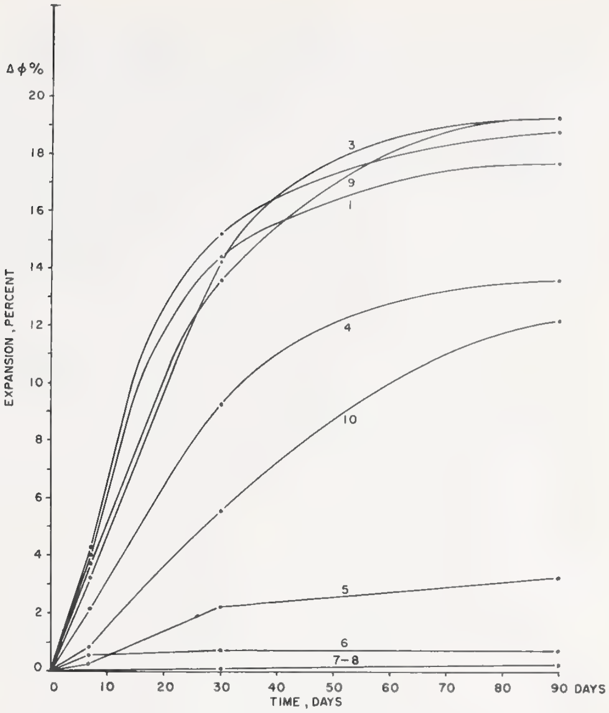

Figure 4. *Expansion of Anstett test specimens.*
Cements: Series 1–10

Already after 7 days, cements B, C, and D show a higher expansion than that of cement A without pozzolanic addition; after 90 days the percentage expansion of cements B and C is four times greater than that of cement A, while that of D is three times greater.

The different expansivity of cement A in comparison with cements B, C, and D and that of cements B and C versus cement D is due to the reactive alumina of pozzolanic material P_2. The lower expansivity of cement D is due to the smaller content of pozzolana P_2 rather than to the presence of pozzolana P_1. In fact the binary cement I containing 10 percent of pozzolana P_1, as cement D, shows a degree of expansion scarcely different from that of cement A without pozzolanic addition.

The low-iron-modulus clinker becomes resistant to the test when 20 percent of pozzolana is added, a result which agrees with the behavior of cements E, F, G, and H.

The results obtained with cements E, F, and I are indicative of the role played by the alumina of pozzolana P_2. Although for the first two cements the amount of reactive alumina supplied by pozzolana is still appreciable, as appears by comparing the values of soluble alumina with the silica/alumina ratio of the three cements (table 3), nevertheless resistance to the test is reached by cement E. On the other hand, for the cement F the reactivity to the sulfate is quite negligible.

As all the soluble alumina of cement I is due to the clinker, and the amount of clinker in cements E and F is only 65 percent against 90 percent for cement I, we can deduce that the alumina in the clinker and the reactive alumina in the pozzolana would not be equivalent as regards the sulfate susceptibility of a pozzolanic cement paste.

Such a conclusion is confirmed by the results obtained for the series 1–10 of the higher-iron-modulus cements. The decisive influence of the alumina in the clinker, compared with that of the reactive alumina in the pozzolana, is shown from the behavior of cements 1, 2, 3, and 9, which, at the different curing ages, present nearly identical expansions. The influence of the clinker composition becomes even more evident for cement 10 which appears highly expansive in contrast to the corresponding cement L in the series prepared with the low-iron-modulus clinker.

Cements 4 and 5, although containing 10 and 15 percent of pozzolana P_1 and 25 and 20 percent of pozzolana P_2 respectively, present a percentage expansion which is of the same order of that of cement 10 for the former, and about half as large for the latter. Cement 6, whose expansivity remains within the limits allowed by the test, demonstrates that the substitution of 15 parts of clinker by 15 parts of pozzolana P_2 is sufficient to allow the 20 parts of pozzolana P_1 to give the resulting cement a good resistance to the test.

The inequivalence of the influence of the reactive alumina in pozzolana and of the alumina in clinker on the sulfate susceptibility of pozzolanic cement pastes cannot be explained, at least at the present stage of knowledge, assuming that the reactive alumina of the pozzolana is combined in a form different from tetracalcium aluminate hydrate, which, together with the ettringite, constitutes, at the shortest curing times, the hydration product of tricalcium aluminate. As was related by Prof. Malquori, the reactive alumina of pozzolana P_2 combines with calcium hydroxide to form tetracalcium aluminate hydrate and the silicoaluminate of Strätling [5]; in the mortars of lime and pozzolana, and in those of pozzolanic cement [6], it was possible to ascertain only the presence of the tetracalcium aluminate hydrate and not that of the silicoaluminate.

The formation of the silicoaluminate is likely to occur in pastes water-cured for a long period, but even if we accept this assumption, which is not important for the aim of our discussion since by the Anstett method the test is carried out on pastes previously cured for only 15 days, it must be remembered that Malquori and Cirilli [7] stated also that the silicoaluminate decomposes in the presence of SO_4^{2-} ions and of $Ca(OH)_2$.

The following assumption appears the most acceptable, and it is furthermore, one of the most probable among those which explain the mechanism of the action of pozzolana P_1 in regard to the behavior of cements in the Anstett test. The reactive alumina and silica of pozzolana are thoroughly mixed in the glass phase, and therefore the product of the lime-alumina reaction will be embodied in the calcium silicate gels, the relative amount of which is much higher.

Recalling the particular geologic nature of pozzolana P_2 [9], there is no plausible reason to suppose a nonhomogeneous distribution of the composition of the glass, at least as regards the insoluble oxides such as silica and alumina. The difficulties met with in the microscopic analysis of the mortars are also evidence that the products of the lime-alumina reaction appear protected by the calcium silicate gels much more than in clinker, where dispersion between calcium silicates and aluminates is undoubtedly lower.

Such assumptions are in accordance with the different sulfate susceptibilities of clinkers of the same composition, but with a different content of glass phase, that is, with different content of crystalline calcium aluminate.

The X-ray examination of the pastes showed that the expansion is in direct relationship with the formation of ettringite. In the nonexpansive cement pastes the three main reflections of ettringite at 9.82, 5.71, and 3.86 A, respectively, are scarcely visible and, for some cements, unnoticeable, while in the pastes of expansive cements ettringite constitutes one of the predominant phases.

In the pastes of pozzolanic cement the very intense reflection of calcium hydroxide at $2\theta=18°$ has a very weak intensity, and in all the pastes with high content in pozzolana P_1 it is completely absent.

Conclusions

On the basis of the results hitherto related, the role of pozzolana P_1, rich in reactive silica, gains a particular importance. The influence of this pozzolana on the behavior of the two series of cements under testing shows two different aspects:

(1) It reduces the reactivity of pozzolanic material P_2 with calcium hydroxide.

(2) It reduces, and at certain ratios suppresses, the sulfate susceptibility of the cement.

The mechanism by which pozzolana P_1 affects the reactivity of pozzolana P_2 depends also on the reaction rate of both materials with calcium hydroxide. Pozzolana P_1 reacts at a higher rate than pozzolana P_2, and it is, therefore, possible to suppose that in a pozzolanic cement containing the two materials the hydrolysis lime is fixed principally by the silica of pozzolana P_1. Then the amount of the newly formed calcium aluminates derived from the alumina of pozzolana P_2 obviously will be lower than in a binary pozzolanic cement containing equal ratios of the same clinker and the same pozzolana.

This conclusion is confirmed by the fact that in the pozzolanic cement under examination, with an addition of 35 percent, the amount of soluble alumina obtained is not proportional to, but is lower than that corresponding to the quantity of the pozzolana P_2 present.

The influence of pozzolana P_1 on the susceptibility of the cement to sulfate attack may be included in what we have already said about the reasons for the inequivalence between the reactive alumina in the pozzolana and the alumina in the clinker.

It seems reasonable to suppose that calcium silicate hydrate gels, produced by the reaction of silica and pozzolana with hydrolysis calcium hydrate, exert an efficient protective action on the aluminates which is probably due to the very low diffusion rate of SO_4^{2-} ions through the gels.

However we cannot exclude the possibility that the stability of aluminates and ettringite in the absence of calcium hydroxide may be endangered by the presence of reactive silica. It is possible that both the above-mentioned assumptions are valid, since the one does not exclude the other, but each requires an experimental confirmation; therefore we are carrying out our investigation in this direction.

At the moment, we would point out particularly the decisive importance of the reactive silica content of the pozzolanic addition, and, in this connection, it is noteworthy that the chemical resistance of pozzolanic cement is closely connected with the relationship that may be established between reactive silica and alumina present in the same cements.

For this reason, such a relationship makes it possible to control the chemical resistance of a pozzolanic cement until it is able to withstand the severe conditions of the Anstett test, which although very far from reproducing the usual attack conditions, is nevertheless significant since it indicates an absolute intrinsic resistance of the binder itself.

From the reported data it would seem that the limited value of the above-mentioned ratio must be about 6 in order that the protective action of the silica become efficient under the conditions of the Anstett test.

Of course, in most cases, it is not necessary to reach such high values, which, however, could be requested for special uses.

It is therefore possible to prepare, by choosing suitable qualities of pozzolanic addition, highly resistant cements of this type. These cements, in this sense, can be compared to high-alumina and supersulfated cements. These particular types of pozzolanic cements have been used industrially in Italy for some years now, with results that may be considered wholly satisfactory.

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Paper VIII–S5. Refractory Barium-Aluminous Cement and Concrete*

Al. Braniski

Synopsis

Part I. Refractory cement. Eight refractory barium-aluminous cements with increasingly improved technological properties were prepared in the laboratory, and their physical, chemical, and mechanical properties were studied.

Certain theoretical and practical considerations concerning their mineralogical constitution are presented. Computation of their potential phase compositions is outlined, and the chemical reactions which take place during the hydration of these new cements are discussed.

The fire resistance of the barium-aluminous cements varies between 1,730 and 1,825 °C, their tensile strengths (at 7 days) vary between 30.4 and 36.9 and their compressive strengths (also at 7 days) between 380 and 445 kg/cm.^{2}

The effect of high temperatures (to 1,300 or 1,400 °C) on the dehydration and cold compressive strength of the hardened (hydrated) barium-aluminous cement was studied, and comparison is made with calcium-aluminous cement, strontium-aluminous cement, barium silicate cement, strontium silicate cement, and portland cement. The refractory barium-aluminous cement is recommended as a suitable cementing material for the production of basic highly refractory concrete.

Part II. Concrete, refractory and highly refractory. Nonrefractory, refractory, and highly refractory concretes were prepared in the laboratory by using white sintered bauxite or wastes of fire-clay, corundum, chrome-magnesite, and magnesite bricks with portland cement (with finely ground admixtures), conventional aluminous cement, white aluminous cement with monocalcium aluminate base, refractory aluminous cement with calcium dialuminate base, and two types of refractory barium-aluminous cement. Study was made of the dependence of refractoriness and resistance to thermal shock of the resulting concretes on the nature of the cement used.

Using the same aggregates and the two refractory barium-aluminous cements in different proportions, a number of refractory and highly refractory concretes were prepared and examined for their more important properties. These refractory and highly refractory concretes exhibit an extraordinary resistance to thermal shock, and the following refractoriness: fire-clay concretes, 1,670 to 1,690 and 1,730 to 1,745 °C, respectively; bauxite concretes 1,750 to 1,790 and 1,790 to 1,825 °C, respectively; corundum concretes 1,865 to 1,910 °C; chrome-magnesite concretes 1,880 to 1,960 °C; and magnesite concretes 1,920 to 1,980 °C.

Also studied were the effect of high temperatures on the dehydration and cold compressive strengths of concretes with refractory barium-aluminous cement, the relation of cold compressive strengths of concretes—uncalcined or calcined at 1,000 or 1,400 °C, respectively—to content of barium-aluminous cement, and the effect of cement content on Seger-cone collapse points of these concretes.

It is concluded that refractory and highly refractory concretes with refractory barium-aluminous cement are greatly superior to those with refractory aluminous cement with calcium dialuminate base, and thus to any refractory or highly refractory concrete made with any other known refractory cement.

Résumé

Première partie: Ciment réfractaire. L'auteur a obtenu au laboratoire huit ciments réfractaires alumineux de baryum aux caractéristiques technologiques graduellement améliorées. Il en étudie leur propriétés physiques, chimiques et mécaniques, fait quelques considérations théoriques et pratiques sur leur constitution minéralogique, sur le calcule de leur composition potentielle ou phasale, ainsi que sur les réactions chimiques qui ont lieu lors de l'hydratation de ces nouveaux ciments.

Les limites des résistances pyroscopiques des ciments réfractaires alumineux de baryum sont 1,730 et 1,825 °C, celles des résistances à la traction (après 7 jours) 30.4 et 36.9 et celles des résistances à la compression (après 7 jours) 380 et 445 kg/cm^2.

L'étude porte encore sur: l'effet des températures élevées (1,300 ou 1,400 °C) sur la déshydratation et les résistances à la compréssion à la température ordinaire du ciment réfractaire alumineux de baryum hydraté, en comparaison avec les ciments alumineux de calcium et de strontium et avec les ciments siliceux de baryum, de strontium et de calcium (ciment portland).

L'auteur recommande le ciment réfractaire alumineux de baryum comme le meilleur liant pour la production des bétons basiques super-réfractaires et réfractaires.

Deuxième partie: Béton réfractaire et super-réfractaire. L'auteur réalise au laboratoire des bétons nonréfractaires, réfractaires et super-réfractaires, en utilisant des agrégats réfractaires de bauxite frittée, de chamotte, de corindon, de chrome-magnésie et de magnésie avec du ciment portland (à ajouts très fins), du ciment fondu, du ciment blanc alumineux à base d'aluminate monocalcique, du ciment réfractaire alumineux à base de dialuminate

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Academia RPR, Bukarest, Rumania.

de calcium, et deux sortes de ciments réfractaires alumineux de baryum. Il en étudie l'effet de la nature du ciment utilisé sur la réfractarité et la résistance aux variations brusques de température de ces bétons.

Utilisant les mêmes agrégats réfractaires et les deux sortes de ciments réfractaires alumineux de baryum en différents quantités, on a obtenu une série de bétons réfractaires et super-réfractaires et étudié leur propriétés spécifiques. Ces bétons réfractaires et super-réfractaires possèdent des résistances exceptionelles aux variations brusques de température et les résistances pyroscopiques suivants: bétons réfractaires à base d'argile 1,670 à 1,690 et 1,730 à 1,745 °C, de bauxite 1,750 à 1,790 et 1,790 à 1,825, de corindon 1,865 à 1,910, de chrome-magnésie 1,880 à 1,960 et de magnésie 1,920 à 1,980 °C.

L'étude porte aussi sur: l'effet des hautes températures sur la déshydratation et les résistances à la compression à la température ordinaire des bétons à ciment réfractaire alumineux de baryum, l'influence de la teneur en ciment réfractaire alumineux de baryum sur les résistances à la compression à la température ordinaire des bétons noncalcinés et calcinés à 1,000 ou 1,400 °C et l'effet de la teneur en ciment sur la résistance pyroscopique de ces nouveaux bétons réfractaires.

Pour conclure l'auteur montre que les bétons réfractaires et super-réfractaires à ciment réfractaire alumineux de baryum sont beaucoup supérieurs aux bétons à ciments réfractaire alumineux à base de dialuminate de calcium et par conséquent aux bétons réfractaires et super-réfractaires à n'importe quel ciment réfractaire connu.

Zusammenfassung

Teil I—Feuerfester Zement. Der Verfasser stellt im Laboratorium acht feuerfeste Barium-Tonerdezemente, mit stetig verbesserten technologischen Merkmalen her, und untersucht einige ihrer physikalischen, chemischen und mechanischen Eigenschaften.

Er macht ferner einige theoretische und praktische Betrachtungen über ihre mineralogische Konstitution, über die Berechnung ihrer potentiellen (phasalen) Zusammensetzung und über die chemischen Reaktionen, welche bei der Hydratation dieser neuen Zemente stattfinden.

Die Feuerfestigkeit der erhaltenen Barium-Tonerdezemente schwankt zwischen 1,730 und 1,825 °C, ihre Zugfestigkeiten (nach 7 Tagen) zwischen 30.4 und 36.9 und ihre Druckfestigkeiten (ebenfalls nach 7 Tagen) zwischen 380 und 445 kg/cm^2.

Der Verfasser untersucht schliesslich den Einfluss hoher Temperaturen (bis 1,300 bzw. 1,400 °C) auf die Entwässerung und die Kaltdruckfestigkeiten des erhärteten (hydratisierten) Barium-Tonerdezementes im Vergleich zum Kalzium-Tonerdezement, Strontium-Tonerdezement, silikatischem Bariumzement, silikatischem Strontiumzement und Portlandzement und empfiehlt den feuerfesten Barium-Tonerdezement als geeignetstes Bindemittel für die Herstellung basischer hochfeuerfester Betone.

Teil II—Feuerfester und hochfeuerfester Beton. Der Verfasser stellt im Laboratorium aus weissem Sinterbauzit bzw. Abfällen von Schamotte-, Korund-, Chrommagnesit- und Magnesitsteinen und Portlandzement (mit fein vermahlenen Zusatzstoffen), gewöhnlichem Tonerdezement, weissem Tonerdezement auf Monokalziumaluminat-Basis, feuerfestem Tonerdezement auf Kalziumdialuminat-Basis und zwei Arten feuerfestem Barium-Tonerdezement als Bindemittel nichtfeuerfeste, feuerfeste und hochfeuerfeste Betone her und untersucht die Abhängigkeit der Feuerfestigkeit und Temperaturwechselbeständigkeit der hergestellten Betone von der Art der als Bindemittel verwendeten Zemente.

Aus denselben Zuschlagstoffen und zwei feuerfesten Barium-Tonerdezementen in verschiedenen Verhältnissen stellt er eine Anzahl feuerfester und hochfeuerfester Betone her und untersucht ihre wichtigsten Eigenschaften. Diese hochwertigen feuerfesten und hochfeuerfesten Betone weisen eine aussergewöhnliche Temperaturwechselbeständigkeit und folgende Feuerfestigkeiten auf: Schamottebetone 1670–1690 bzw. 1,730–1,745 °C, Bauxitbetone 1,750–1,790 bzw. 1,790–1,825 ° C, Korundbetone 1,865–1,910 °C, Chrommagnesitbetone 1,880–1,960 und Magnesitbetone 1,920–1,980 °C.

Der Verfasser untersucht ferner den Einfluss hoher Temperaturen auf die Entwässerung und Kaltdruckfestigkeiten der Betone aus feuerfestem Barium-Tonerdezement, die Abhängigkeit der Kaltdruckfestigkeiten der ungebrannten und bei 1000 bzw. 1400 °C gebrannten Betone vom Barium-Tonerdezementgehalt und den Einfluss des Zementgehaltes auf den Segerkegel-Fallpunkt dieser Betone.

Er stellt schliesslich fest, dass der hochfeuerfeste Beton aus feuerfestem Barium-Tonerdezement dem hochfeuerfesten Beton aus feuerfestem Tonerdezement auf Kalziumdialuminat-Basis, und somit auch jedem feuerfesten oder hochfeuerfesten Beton aus anderem bekannten, feuerfesten Zement, weit überlegen ist.

Part I. Refractory Cement

Introduction

Conventional cements—portland cement and aluminous cement—are nonrefractory hydraulic cementing materials (they soften and even fuse below 1,580 °C). When a high-strength refractory concrete is desired, preference is given to *refractory* hydraulic binders, such as refractory aluminous cement with calcium dialuminate base or refractory barium-aluminous cement [1].[1]

Refractory aluminous cements with calcium dialuminate base [2] were studied in 1943 in the

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[1] Figures in brackets represent the literature references at the end of this paper.

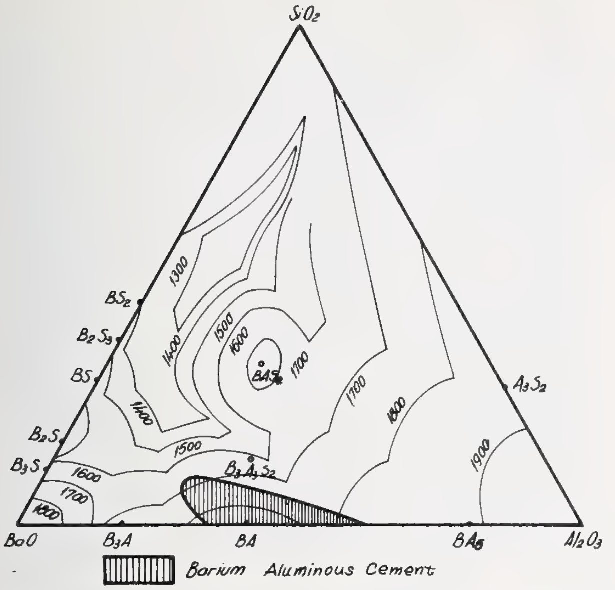

Figure 1. *Position of refractory barium-aluminous cement in the ternary system: barium oxide-alumina-silica, according to Toropov, Galachov, and Bondar-Braniski.*

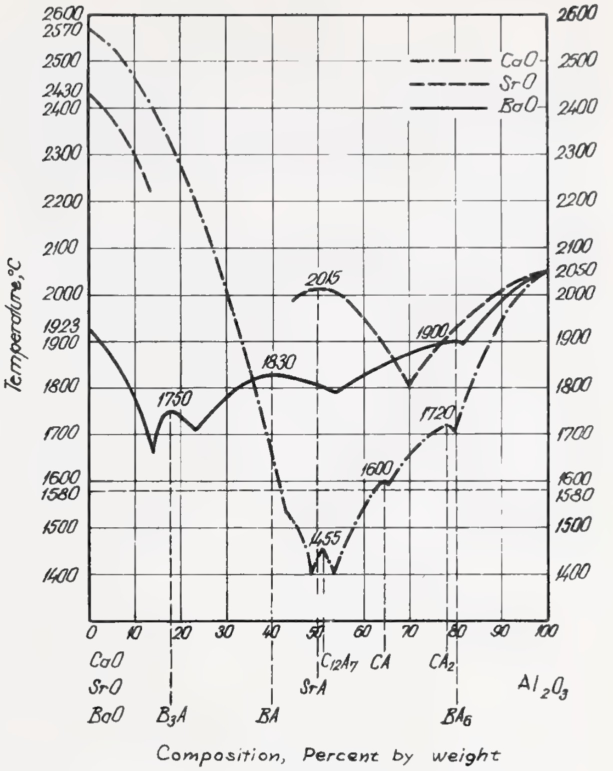

Figure 2. *Comparative diagram of the binary systems:* $CaO\text{-}Al_2O_3$, $SrO\text{-}Al_2O_3$, *and* $BaO\text{-}Al_2O_3$.

United States of America and were produced industrially in England and France by 1950.

Barium-aluminous cements [1] are ordinary aluminous cements in which calcium oxide is replaced by barium oxide. The clinker is burned to sintering or fusion.

When these cements contain fluxing materials (iron oxide, silica, magnesia, soda, and potassa) in only very small quantities, they become *refractory* barium-aluminous cements with a fire resistance between 1,730 and 1,825 °C.

Figure 1 shows the location of refractory (without flux) barium-aluminous cement in the ternary system: barium oxide-alumina-silica [3] according to Toropov, Galachov, and Bondar-Braniski.

The diagram shows that the point of fusion, i.e., collapse of the Seger cone, of a refractory barium-aluminous cement is higher the closer its chemical composition approaches that of monobarium aluminate, BA.

Figure 2 presents a comparison of three binary systems: the system lime-alumina, according to Rankin and Wright [4], corrected by recent writers; the system strontium oxide-alumina according to Wartenberg and Reusch [5]; and the system barium oxide-alumina according to Toropov and Galachov [6].

The calcium, strontium, and barium aluminous cements show the alkaline earth monoaluminates as characteristic components.

Figure 2 shows that strontium monoaluminate, SrA, and barium monoaluminate, BA, have much higher fusion points than calcium monoaluminate, CA, or calcium dialuminate, CA_2.

Consequently, the strontium- and barium-aluminous cements must be considerably more fire-resistant than the corresponding calcium-aluminous cement, a fact which is proved experimentally every time a comparison is made.

Experimental Procedure

Raw Materials for the Manufacture of a Refractory Barium-Aluminous Cement

Synthetic barium carbonate and barium sulfate, as well as alumina and fire clay, were used to produce refractory barium-aluminous cements. The chemical compositions of these raw materials are given in table 1.

Table 1. *Chemical compositions of raw materials used*

	Synthetic barium carbonate	Synthetic barium sulfate	Industrial alumina	Fire clay
	Percent	*Percent*	*Percent*	*Percent*
SiO_2			0.66	67.85
Al_2O_3			98.60	20.37
Fe_2O_3			.11	3.24
CaO			.46	.82
$BaCO_3$	98.10			
$BaSO_4$		99.82		
BaS	.81	.01		
MgO			.24	.43
Alkalies			.77	.57
Loss on ignition				6.72
Insoluble in HCl	.76			

Procedure in Synthesizing Refractory Barium-Aluminous Cement

The synthesis of barium-aluminous cement [1] is identical with that of conventional (calcium) aluminous cement, with the only difference that the burning temperature of the clinker is somewhat higher, thus causing a number of operational difficulties.

Cooling of cement clinker should not be rapid, as highest mechanical strengths are obtained with cements ground from slowly cooled clinker.

The finely ground materials were combined in specified proportions and homogenized in a dry state. Burning of the samples was carried out at temperatures between 1,580 and 1,630 °C, depending on the composition of the mix. Duration of burning amounted to 7 to 8 hr, of which 5 to 6 hr were spent in raising the temperature and 2 hr at maximum temperature.

The temperature was controlled by means of an optical pyrometer and Seger cones 26, 27, and 28.

Considerations on Refractory Barium-Aluminous Cements

Refractory barium-aluminous cements consist mainly of a large proportion of monobarium aluminate, $BaO \cdot Al_2O_3$, and a small proportion of dibarium silicate, $2BaO \cdot SiO_2$.

According to Wartenberg and Reusch, there exists only one barium aluminate, monobarium aluminate; according to Toropov, there are three, namely: tribarium aluminate, $3BaO \cdot Al_2O_3$, monobarium aluminate, $BaO \cdot Al_2O_3$, and barium hexaluminate, $BaO \cdot 6Al_2O_3$.

The binary system $BaO–Al_2O_3$ was studied in part by Wartenberg and Reusch [5], and in detail by Toropov and Galachov [6], and by Lagerqvist, Wallmark, and Westgren [7].

A comparison (fig. 2) of the diagrams of the system $BaO–Al_2O_3$, presented by Toropov and Galachov [6], of the system $SrO–Al_2O_3$ by Wartenberg and Reusch [5], and of the system $CaO–Al_2O_3$ by Rankin and Wright [4], shows that not very basic barium aluminates, of the type of barium monoaluminate and barium hexaluminate and their mixtures, in general have a much higher point of fusion, or higher fire resistance, than the respective calcium aluminates.

The regions around barium monoaluminate and calcium dialuminate correspond to refractory barium-aluminous cements and refractory calcium-aluminous cements.

We deduce further, that production of barium-aluminous cements with a base of barium aluminates of a higher alumina content than monobarium aluminate is of little significance, quite in contrast to calcium aluminous cement, for which the industrially produced aluminous cement with calcium dialuminate base results in increased fire resistance and represents a considerable advance.

Computation of the mineralogical (potential or phase) composition of a refractory barium-aluminous cement on the basis of its chemical analysis proceeds in accordance with Bogue's well-known method [8] for the portland cements, or according to Parker's special method [9] for conventional (calcium) aluminous cements, with the aid of simple mathematical formulae, derived on the basis of an assumed sequence of formation of the mineralogical components.

As refractory barium-aluminous cements, produced by sintering in an oxidizing atmosphere, contain very little Fe_2O_3 and hardly any FeO, one can ignore the possibility that clinkers of iron-containing aluminous cements will contain hexacalcium tetraluminate ferrosilicate, $6CaO \cdot 4Al_2O_3 \cdot FeO \cdot SiO_2$, and hexacalcium tetraluminate magnesium silicate, $6CaO \cdot 4Al_2O_3 \cdot MgO \cdot SiO_2$, two compounds discovered by Parker [9], and can assume the entire iron content to be in the Fe_2O_3 state.

Considering that alkali oxides Na_2O and K_2O become volatilized below 1,350 °C, one can assume the following sequence for the computation of the mineralogical components of refractory barium-aluminous cement:

1. tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$;
2. tetrabarium aluminoferrite, $4BaO \cdot Al_2O_2 \cdot Fe_2O_3$;
3. gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$;
4. dibarium silicate, $2BaO \cdot SiO_2$;
5. monocalcium aluminate, $CaO \cdot Al_2O_3$, and
6. monobarium aluminate, $BaO \cdot Al_2O_3$.

When there is an excess of Al_2O_3, an additional formation of a certain quantity of barium hexaluminate $BaO \cdot 6Al_2O_3$ may take place, according to Toropov [6] or of $3BaO \cdot 16Al_2O_3$, according to Lagerqvist [7]; additional formation of tribarium aluminate, $3BaO \cdot Al_2O_3$, may occur if there is excess BaO.

Barium dialuminate, $BaO \cdot 2Al_2O_3$ (corresponding to a calcium dialuminate $CaO \cdot 2Al_2O_3$) does not appear to exist. Its existence is confirmed by neither Toropov nor Lagerqvist.

Swayze [10] and other researchers have proved that tetracalcium aluminoferrite, known as brownmillerite, does not exist as a chemical compound, but only as a component of a series of solid solutions between the following chemical compounds: the hypothetical dicalcium aluminate, $2CaO \cdot Al_2O_3$, and dicalcium ferrite, $2CaO \cdot Fe_2O_3$, or between the given chemical compounds hexacalcium dialuminoferrite, $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$, and hexacalcium aluminodiferrite, $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$.

However, as the computation formulas for the mineralogical components of the cements are derived on the basis of tetracalcium aluminoferrite, it and tetrabarium aluminoferrite, $4BaO \cdot Al_2O_3 \cdot Fe_2O_3$, are treated as present.

In the following text we use: $S=SiO_2$; $A=Al_2O_3$; $F=Fe_2O_3$; $C=CaO$; and $B=BaO$. According to whether less or more than 4 molecules of CaO per molecule of Fe_2O_3 are present in the cement, two cases are distinguished in computing the mineral components (potential composition) of barium-aluminous cements from the chemical analysis.

In the first case, the lime is computed as tetracalcium aluminoferrite, C_4AF. From the remainder of the iron oxide one computes the content of tetrabarium aluminoferrite, B_4AF.

There follows a computation of dibarium silicate, B_2S, equivalent to all the silica, and computation of monobarium aluminate, BA, and additional tribarium aluminate, B_3A (if there is excess barium oxide), or additional barium hexaluminate, BA_6 (if there is excess alumina).

In the second case, the entire iron-oxide content is computed as tetracalcium aluminoferrite, C_4AF, and the excess lime as gehlenite, C_2AS, insofar as silica is available.

If there is residual free lime one computes the corresponding content of monocalcium aluminate, CA, without computing any dibarium silicate B_2S. Finally one computes the content of the main cement constituent, monobarium aluminate, BA, with, as the case may be, some additional tribarium aluminate, B_3A, or barium hexaluminate, BA_6.

When free lime is not sufficient for complete conversion of the silica to gehlenite, one computes, up to full silica utilization, the content of dibarium silicate, B_2S, and, subsequently, the content of monobarium aluminate, BA, with accompanying barium hexaluminate, BA_6, or tribarium aluminate, B_3A.

For computing the potential (phase) composition of barium-aluminous cement, the computation formulae, establishing the percentages of the various mineralogical components, are derived as for portland cement [8].

Synthesized Barium-Aluminous Cements and Their Properties

Using 5 parts of industrial alumina, 14.5 parts of synthetic barium carbonate, and 1.5 parts of refractory clay, or 5 parts industrial alumina, 17.5 parts industrial barium sulfate, and 1.5 parts by weight of refractory clay, of the compositions given in table 1, we produced two refractory barium-aluminous cements with identical technological properties (refractoriness 1,730 °C=SK 33), of which the first has the following chemical composition: 5.99 percent SiO_2, 29.60 percent Al_2O_3, 0.31 percent Fe_2O_3, 0.20 percent CaO, 63.53 percent BaO, 0.10 percent MgO, and 0.27 percent alkali oxides. (This cement is designated II in table 4.)

Computation of potential composition of refractory barium-aluminous cement II

(Molecular weights: SiO_2, 60.06; Al_2O_3, 101.92; Fe_2O_3, 159.68; CaO, 56.07; BaO, 153.36)

	Compute:	5.99 SiO_2+	29.60 Al_2O_3+	0.31 Fe_2O_3+	0.20 CaO+	63.53 BaO	to the following potential composition
0.20	CaO combines with		0.09 Al_2O_3+	0.14 Fe_2O_3	--------	--------	giving 0.43 C_4AF
	Remainder		29.51 Al_2O_3	0.17 Fe_2O_3	--------	--------	
0.17	Fe_2O_3 combines with		0.11 Al_2O_3	--------		and 0.65 BaO	giving 0.93 B_4AF
	Remainder		29.40 Al_2O_3	--------		62.88 BaO	
5.99	SiO_2 combines with	--------				30.59 BaO	giving 36.58 B_2S
	Remainder	--------		--------		32.29 BaO	
32.29	BaO combines with		21.46 Al_2O_3			--------	giving 53.75 BA
	Remainder	--------	7.94 Al_2O_3	--------		--------	
7.94	Al_2O_3 combines with		--------				4.00 BA giving 11.94 BA_6
	Remainder	--------	--------	--------		--------	49.75 BA giving 49.75 BA

Another refractory barium-aluminous cement was produced from one part industrial clay and two parts by weight synthetic barium carbonate. Its chemical composition is 0.68 percent SiO_2, 39.61 percent Al_2O_3, 0.24 percent Fe_2O_3, 0.37 percent CaO, 58.73 percent BaO, 0.15 percent MgO, and 0.22 percent alkali oxides.

Computation of potential composition of refractory barium-aluminous cement I

	Compute:	0.68 SiO_2+	39.61 Al_2O_3+	0.24 Fe_2O_3+	0.37 CaO+	58.73 BaO	to the following potential composition
0.24	Fe_2O_3 combines with		0.15 Al_2O_3	--------	and 0.34 CaO		giving 0.73 C_4AF
	Remainder		39.46 Al_2O_3	--------	0.03 CaO		
0.03	CaO combines with	0.02 SiO_2	0.03 Al_2O_3	--------	--------		giving 0.08 C_2AS
	Remainder	0.66 SiO_2	39.43 Al_2O_3	--------	--------		
0.66	SiO_2 combines with	--------				3.37 BaO	giving 4.03 B_2S
	Remainder	--------		--------	--------	55.36 BaO	
55.36	BaO combines with		36.80 Al_2O_3			--------	giving 92.16 BA
	Remainder	--------	2.63 Al_2O_3	--------	--------	--------	
2.63	Al_2O_3 combines with		--------				1.31 BA giving 3.94 BA_6
	Remainder	--------	--------	--------	--------	--------	90.85 BA giving 90.85 BA.

The setting time and soundness of this refractory barium-aluminous cement are normal, its refractoriness is 1810 °C, and its mechanical strengths at 7 and 28 days, respectively, in kg/cm^2 are : tensile strength—34.8 and 37.5 respectively, compressive strength—416 and 462 respectively.

As it was established that monobarium aluminate has excellent setting properties, has normal set, and hardens very rapidly in the first 24 hours, as is the case with ordinary calcium-aluminous cement, and, in addition, that silica acts as a fluxing agent, a series of five refractory barium-aluminous cements were prepared of pure raw materials with monobarium aluminate as base and with decreasing silica content. In this manner the refractoriness of these cements can be increased by 120 °C, as shown by table 2.

It was also established that the less silica contained in the cement, the faster the set.

In accordance with the viewpoint of Jules Bied [11], the discoverer of calcium-aluminous cement (ciment fondu), cement A was designed to consist of 2 moles of monobarium aluminate and 1 mole of dibarium silicate. Bied holds that the ordinary aluminous cement should have the following chemical composition:

$$2(\mathrm{CaO{\cdot}Al_2O_3})+2\mathrm{CaO{\cdot}SiO_2}$$

Cements A, B, C, D, and E have a steadily decreasing silica content (from 7 to 1 percent), and this corresponds to an increase in monobarium aluminate content from 58 to 94 percent and a drop in dibarium silicate content from 42 to 6 percent. Dibarium silicate acts as a fluxing agent with respect to the highly refractory monobarium aluminate. This fact explains why a drop in dibarium silicate, i. e., in silica content, raises the fire resistance of a cement from 1,750 to 1,825 °C. It follows that fire resistance of barium-aluminous cement increases the more its chemical composition approaches that of monobarium aluminate (with as little silica, iron oxide, magnesium oxide, and alkalies as possible).

However, a low silica content of about 1 percent improves the sintering and reduces the fire resistance of cement by only 50 °C.

As monobarium aluminate and dibarium silicate form far below their fusion temperature, fire-resistant barium-aluminous cements of good quality can be produced by burning at temperatures of incomplete sintering, but above 1,450 °C, on condition that the raw materials used are very finely ground and thoroughly homogenized. It is recommended to cool the cement clinker slowly.

Refractory barium-aluminous cements A, B, C, D, and E, are water soluble. Their solubility in water increases (from cement A to cement E) with decreasing SiO_2, or $2BaO{\cdot}SiO_2$, content and increasing $BaO{\cdot}Al_2O_3$ content, which is natural, as the latter represents the soluble component of the cement.

Tensile and compressive strengths of these cements in kg/cm² at 7 days are given in table 3, their fire resistance in table 2.

Tables 2 and 3 show that the mechanical strengths of refractory barium-aluminous cements are higher the greater their content of monobarium aluminate. Refractory barium-aluminous cements require a much smaller quantity of water for hardening than calcium-aluminous cements.

Due to the high solubility of barium aluminates, the setting and hardening processes of refractory barium-aluminous cements are extremely complex. To investigate them is therefore much more difficult than with ordinary calcium-aluminous cements.

Table 2. *Chemical composition, mineralogical components, and refractoriness of some barium-aluminous cements*

Cement	A	B	C	D	E
SiO_2 *percent*	7.0	5.0	3.0	2.0	1.0
Al_2O_3 *percent*	23.2	28.0	32.8	35.2	37.6
BaO *percent*	69.8	67.0	64.2	62.8	61.4
Monobarium aluminate, $BaO{\cdot}Al_2O_3$ *percent*	58	70	82	88	94
Dibarium silicate, $2BaO{\cdot}SiO_2$ *percent*	42	30	18	12	6
Refractoriness *°C*	1,750	1,770	1,790	1,810	1,825

Table 3. *Tensile and compressive strengths of some barium-aluminous cements*

Cement	Tensile strength	Compressive strength
	kg/cm²	*kg/cm²*
A	30.4	380
B	29.6	386
C	33.7	401
D	35.4	432
E	36.9	445

The basic reactions of chemical hydration of refractory barium-aluminous cements consist primarily of the hydration reactions of monobarium aluminate and, secondarily, the hydration reactions of dibarium silicate.

Hydration of monobarium aluminate proceeds as follows:

$$\mathrm{BaO{\cdot}Al_2O_3+6H_2O=BaO{\cdot}Al_2O_3{\cdot}6H_2O}$$

$$\mathrm{2(BaO{\cdot}Al_2O_3{\cdot}6H_2O)=2BaO{\cdot}Al_2O_3{\cdot}9H_2O+2Al(OH)_3}$$

$$\mathrm{2BaO{\cdot}Al_2O_3{\cdot}9H_2O+BaO{\cdot}Al_2O_3=3BaO{\cdot}Al_2O_3{\cdot}6H_2O+2Al(OH)_3.}$$

There is early formation of a large quantity of aluminum hydroxygel or hydrated alumina, in the form of gibbsite ($2Al(OH)_3{=}Al_2O_3{\cdot}H_2O$), which produces an early hardening of cement, with attendant formation of dibarium and tribarium hydroaluminate.

The end products of the hydration process are, accordingly, gels of alumina trihydrate and tribarium aluminate hexahydrate.

Dibarium silicate hydrates much more slowly than monobarium aluminate, according to the reactions:

$$\mathrm{2BaO{\cdot}SiO_2+}n\mathrm{H_2O=2BaO{\cdot}SiO_2{\cdot}}n\mathrm{H_2O}$$

$$\mathrm{2BaO{\cdot}SiO_2{\cdot}}n\mathrm{H_2O=BaO{\cdot}SiO_2{\cdot}}(n-1)\mathrm{H_2O+Ba(OH)_2}$$

Hydrated monobarium silicate contributes during drying (gradual dehydration) to a slow hardening of the cement, as does barium hydroxide, which is readily changed to barium carbonate by contact with the carbon dioxide of the atmosphere.

Cement C was investigated under the microscope before and during hydration.

Thin sections of this cement clinker showed two different phases under the microscope. The first phase consists of isotropic, refractive particles with a glassy appearance. This phase constitutes 80 to 85 percent of the whole and consists of small crystals of white monobarium aluminate.

The second (secondary, 15–20 percent) phase consists of small birefringent dibarium silicate crystals with a higher refractive index.

Concerning the effect of water on this cement, it was established that soon after initial contact with water part of the cement grains dissolve to form an amorphous gel mass.

Ten to twelve hours after formation of the amorphous gel mass from the hydrated alumina there appears in several places under the microscope a series of very small white crystals of tribarium aluminate hexahydrate.

Dehydration of refractory barium-aluminous cement by heating to high temperatures is a very complicated process, which brings about a reduction in mechanical strength and a gradual decomposition of the hardened cement. It takes place at lower temperatures if the temperature increase is slow and the heating is prolonged; and the dehydration thus depends primarily on temperature and, secondarily, on the duration of heating.

Prolonged heating at a lower temperature can, consequently, result in greater impairment of strength in refractory concrete than a shorter heating at a higher temperature.

After 170 hr of heating at 400 to 420 °C, the hardened barium-aluminous cement loses about 92 percent of its original water. The remaining 8 percent is very strongly held and can be driven off only after a very long period of heating at temperatures above 800 °C.

Effect of Higher Temperatures on the Dehydration of Hardened (Hydrated) Refractory Barium-Aluminous Cement

Dehydration of hardened refractory barium-aluminous cement was studied by comparison with conventional (calcium) aluminous cement, strontium-aluminous cement, barium silicate cement, portland cement (calcium silicate cement), and strontium silicate cement, namely, by simultaneous heating of 100-g samples to different constant temperatures.

Heating to 105 °C was carried out in an electrically heated cabinet; further heating to 1,300 °C followed in an electric furnace with silicon carbide rods with automatic temperature control for maintenance of constant burning temperature.

The same specimens were subjected to heating at increasingly higher temperatures.

The water required for setting and hardening of the cements is taken as unity (100 percent) and the various weight losses in grams, obtained by successive weighings, are computed in percent.

The weight losses of hardened (hydrated) cements at increasingly higher, constant burning temperatures are expressed in percent in figure 3.

As can be seem, maximum water loss takes place for all cements below 105 °C, and, indeed, for all aluminous cements (calcium, strontium, barium) to a much greater degree than for silicate cements (portland, strontium, and barium cement). A very pronounced dehydration occurs at the time when "water of constitution" (chemically bound water) is withdrawn from the mineralogical cement components. This happens for calcium- and strontium-aluminous cements between 200 and 400 °C, for barium-aluminous cement between 200 and 500 °C and for silicate cements much later, namely, between 500 and 700 °C for portland cement, between 600 and 800 °C for strontium cement and between 700 and 900 °C for barium cement.

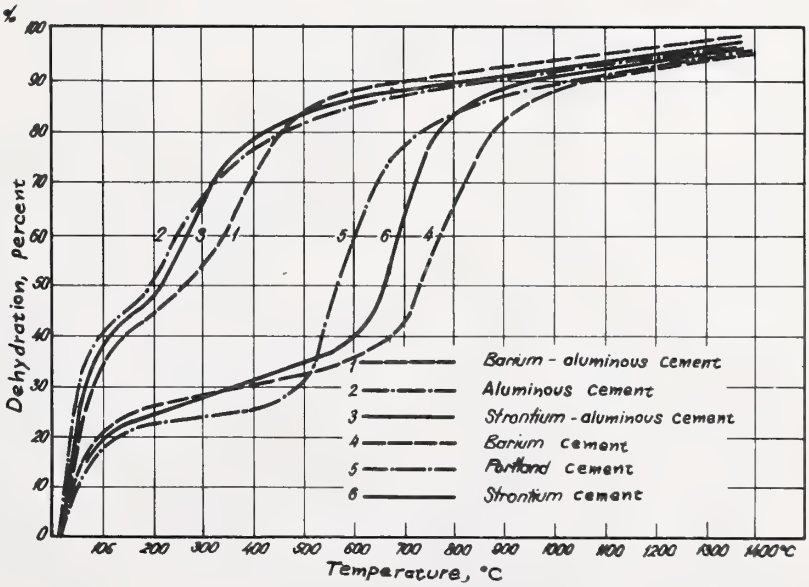

FIGURE 3. *Cement dehydration in percent at different burning temperatures.*

Cold Compressive Strength of Hardened Refractory Barium-Aluminous Cement as a Function of Heating to High Temperatures

Studies involved a comparison between conventional (calcium) aluminous cement, strontium-aluminous cement, barium silicate cement, strontium silicate cement, and portland cement. The 28-day compressive strengths of unheated specimens were taken as a basis of reference (100 percent).

Six-hour heating to constant temperatures proceeded simultaneously for all specimens, namely, to 105 °C in an electric heating cabinet, to temperatures between 300 and 1,300 °C in an electric furnace with silicon carbide rods, and to 1, 400 °C in a laboratory furnace heated with methane gas.

Figure 4 shows that the cold compressive strengths increase by heating to 105 °C, decrease as the temperature is raised, and increase again at 750 °C or 850 to 950 °C, respectively.

According to this, there takes place a partial destruction of the structure of hydrated cement through withdrawal of chemically combined water, followed (during sintering) by a "ceramic strengthening" of the dehydrated dissociation components, with accompanying gain in the corresponding cold compressive strengths of the cements in question.

When burned beyond 1350 °C the cold compressive strengths of all cements exceed their initial values.

The smallest decrease in cold compressive strength is exhibited by barium-aluminous cements, and the largest loss by strontium silicate cement. In general, aluminate cements (barium-, strontium-, and calcium-aluminous cement) show smaller maximum strength losses through heating to higher temperatures than do silicate cements (barium, strontium, and portland cement). Thus, in this respect also, aluminous cements (as binding materials for fire-resistant concrete) have an advantage over silicate cements.

Conclusion

1. Fire resistance (refractoriness) and mechanical strength of refractory barium-aluminous cement are higher the more its chemical composition approaches that of monobarium aluminate, i.e., the lower its content of silica, iron oxide, alkalies, etc., as impurities.

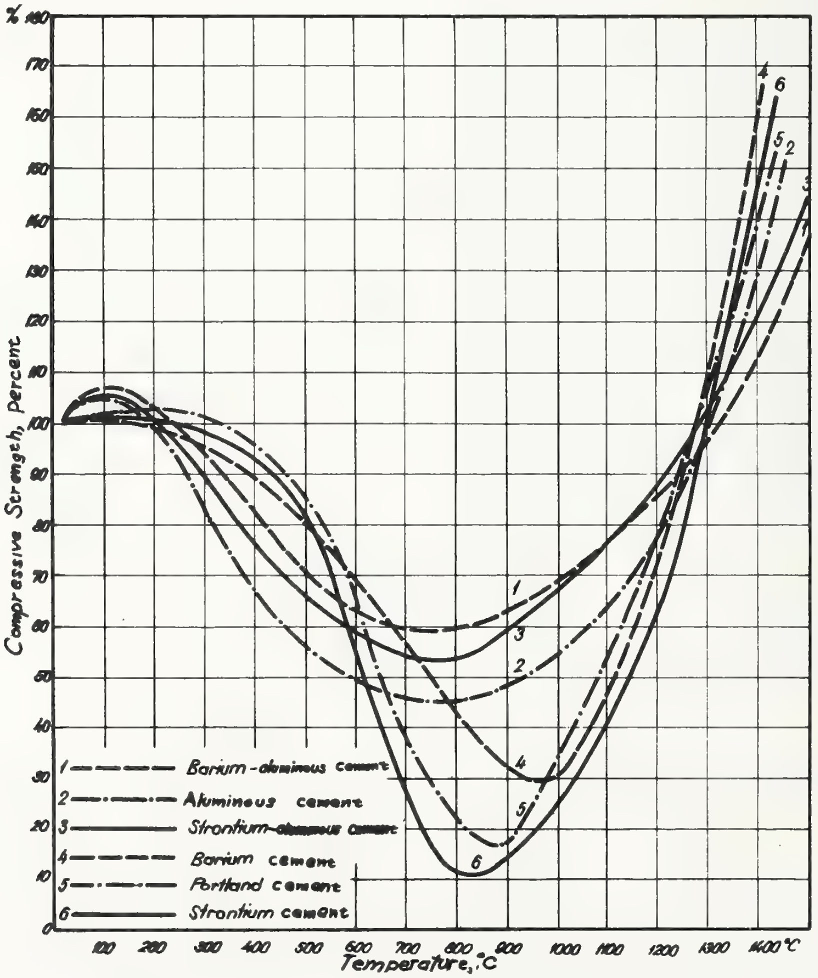

FIGURE 4. *Cold compressive strengths of cements following 6-hr heating to different temperatures.*

2. Refractory barium-aluminous cement fuses with much greater difficulty than the familiar refractory calcium-aluminous cement manufactured with calcium dialuminate base.

3. The setting and hardening properties of barium-aluminous cement are normal; its strengths are exceptionally high after a few hours. Thus barium-aluminous cement is a high-early-strength cement, similar to calcium- and strontium-aluminous cements.

4. In contrast to other cements, barium-aluminous cement is highly water soluble. Thus it is basically not a hydraulic, but an air-hardening cementing material.

5. Hardening of hydrated refractory barium-aluminous cement is produced, first, through the drying of hydrated alumina gel and, second, through the drying of the gels of the hydrated barium-aluminates and barium silicates or crystallization of tribarium-aluminate hexahydrate.

6. Of all known cements, refractory barium-aluminous cement shows the least loss of cold compressive strength through heating to high temperature.

7. On the basis of all the data presented here, refractory barium-aluminous cement is best suited for use in basic highly refractory concrete.

Part II. Concrete, Refractory and Highly Refractory

Introduction

By definition, a refractory concrete is a structural material consisting of a hydraulically hardening cement and suitable refractory aggregate whose Seger cone collapse lies above SK 26 (1,580 °C). A highly refractory concrete is characterized by SK over 36 (1,790 °C).

A highly refractory concrete is a structural material produced without burning, through a chemical bonding in the cold of highly refractory aggregates by means of a refractory cementing material. It differs from "nonburned highly refractory products," which are also denoted "chemically bonded highly refractory structural materials," in that it is a monolithic (jointless) highly refractory product produced *in situ*. Curt Platzmann took out the first patent for the manufacture of refractory concrete in 1922 in Germany. This concrete was resistant only up to 1,000 to 1,100 °C and consisted of coarsely granular fire clay (schamotte) and portland cement with addition of trass or some other finely ground siliceous admixture as binder. Portland cement without such an admixture was proven unsuitable, as the lime liberated during setting remains uncombined and reacts with the moisture of the air during cooling of the concrete to produce undesirable (destructive) unsoundness.

In 1949 in the USSR K. D. Nekrasov [12] brought to a conclusion the study and commercial production of the fire-resistant, but not truly refractory (fire-stable), concrete made with portland cement and ground admixtures.

P. Kestner [13] produced in 1926 the first—inappropriately called—"refractory" concrete made with calcium-aluminous cement (ciment fondu).

In 1934 Braniski [14] reported in a paper on "so-called refractory cements" that all previously known refractory cements, mortars and concretes were in reality not refractory, but only fire resistant to a limited extent, since they could not withstand temperatures above 1,580 °C.

The properties and method of manufacture of refractory aluminous cement concrete formed the subject of studies by Coss and Cent [15], Czernin [16], Hussey [17], Lepingle [18], Möser [19], Giles [20], Williams [21], Robson [22], Wygant and Bulkley [23] and other research workers. Lehmann and Mitusch [24] demonstrated recently that the behavior of refractory calcium-aluminous cement concrete at high temperatures should be interpreted on the basis of its chemical composition, and they derived a number of rules defining the composition of refractory aluminous fused-cement concrete adapted to the requirements of the times.

Figure 5 shows that even when basic highly refractory aggregates are used, highly refractory concrete can be obtained only when it contains *refractory* aluminous cement such as, for example, refractory (no iron oxide) barium-aluminous cement or refractory calcium-aluminous cement with calcium dialuminate base. The latter has been manufactured in France since 1950.

The purpose of the present work is to establish the relation of refractoriness and resistance to thermal shock of concrete (with identical aggregates, grading, degree of compaction, and consistency) to the nature of the cements used, and to examine the more important properties of refractory and highly refractory concrete made with refractory barium-aluminous cements.

Experimental Procedure

Raw Materials Used in the Preparation of the Nonrefractory, Refractory, and Highly Refractory Concretes That Were Studied

Six cements were used in the preparation of the concretes investigated: one portland cement, one conventional high-iron-oxide aluminous cement (ciment fondu), one white aluminous cement with monocalcium aluminate base, one refractory aluminous cement with calcium dialuminate base (of the type produced commercially), and two refractory barium-aluminous cements.

The chemical composition and refractoriness of these cements are given in table 4.

The properties and method of preparation of the two refractory barium-aluminous cements I and II are described in part I of this paper.

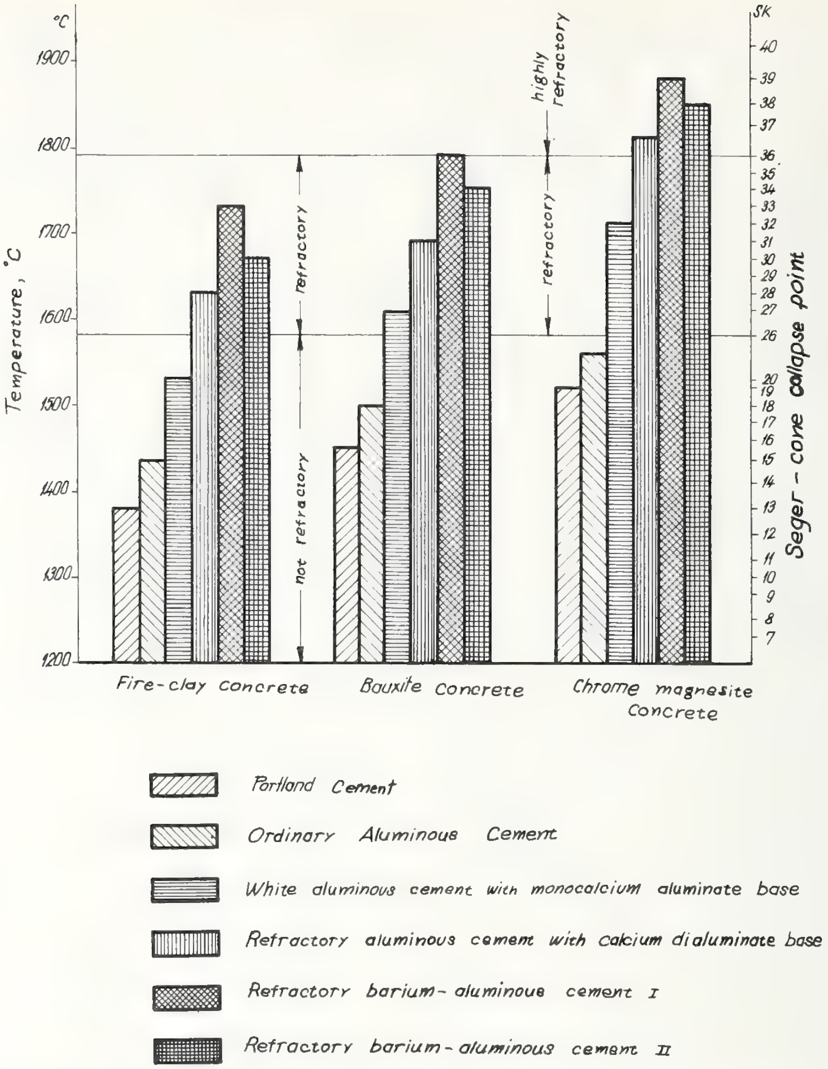

FIGURE 5. *Seger-cone collapse of fire-clay, bauxite, and chrome-magnesite concretes with different cements as binders.*

TABLE 4. *Chemical composition and refractoriness of the cements used*

[Percent]

	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
SiO_2	21.43	4.23	0.45	0.34	0.68	5.99
Al_2O_3	5.71	37.18	61.81	72.73	39.61	29.60
Fe_2O_3	3.64	17.35	0.41	0.21	0.24	0.31
CaO	63.32	36.49	33.56	26.49	.37	.20
BaO	-----	-----	-----	-----	58.73	63.53
MgO	1.18	0.66	0.56	0.28	0.15	0.10
Alkalies	-----	-----	-----	-----	.22	.27
SO_3	1.69	-----	-----	-----	-----	-----
Insoluble	1.78	3.81	.25	.18	-----	-----
Loss on ignition	1.57	0.42	-----	-----	-----	-----
Total	100.32	100.14	100.04	100.23	100.00	100.00
Refractoriness						
°C	1,350	1,250	1,520	1,610	1,810	1,730
Sk	12	8	19	27	36/37	33

The following refractory aggregates were used: white sintered bauxite and wastes of fire clay (schamotte), corundum, chrome-magnesite, and magnesite brick. Their more important properties are given in table 5.

Table 6 presents the chemical composition of white sintered bauxite and firebrick wastes.

TABLE 5. *Properties of refractory aggregates used*

Technological properties	Aggregates				
	Fire-brick wastes	White sintered bauxite	Corundum brick wastes	Chrome-magnesite brick wastes	Magnesite brick wastes
Refractoriness *°C*	1,750	1,850	1,930	>2,000	>2,000
Collapse of Seger cone	34	38	40	>42	>42
Cold compressive strength *kg/cm²*	180	240	385	545	694
Apparent porosity *percent*	24	21	17	22	18
Weight per unit volume *g/cm³*	2.00	2.30	3.35	3.05	2.95
Resistance to thermal shock *cycles*	53	42	23	8	6

TABLE 6. *Chemical composition of firebrick wastes and white sintered bauxite*

[Percent]

Chemical composition	Firebrick wastes	White sintered bauxite
SiO_2	58.57	13.61
Al_2O_3	38.42	78.34
Fe_2O_3	2.35	5.85
CaO	.43	.96
MgO	Trace	.64
Alkalies	.47	.60
Total	100.24	100.00

Procedure for the Production of Concrete

In general the preparation of the concretes investigated here was the same as for conventional concrete.

The consistency of the concrete must be plastic, and the concrete should be as well compacted as possible. It is advisable not to wet in advance any porous aggregates, or to wet them only slightly, and to mix them in the dry or semidry condition.

The mechanical strengths of concretes depend—aside from cement content—on the quantity of mixing water and grading of the aggregates.

Too large a quantity of mixing water will produce porous concrete with reduced mechanical strenth. Too little water prevents complete hydration of the cement. An optimum quantity of mixing water should be used, which varies from case to case depending on the nature of the aggregates and the cement.

The particle size and, particularly, the maximum permissible diameter of the aggregate, varies with the thickness of a monolithic lining of refractory concrete. It should not exceed ⅕ of the thickness of the concrete. The grading should, in general, be as follows: 50 percent coarse size, 10 percent medium size, and 40 percent fine size (0–0.2mm).

The normal cement content is 10 to 20 percent of the total dry weight of the mix. The dry fine aggregate is mixed with the required quantity of cement and homogenized completely. Only then are the dry or semidry medium and coarse sizes added, followed by another mixing and homogenizing.

The required amount of water is added at the end and thoroughly mixed in. The plastic refractory concrete is then placed in the mold without delay and tamped.

One should take care that the setting and hardening of concrete during the first three days takes place in a wet atmosphere. To this end, it is cured under wet cloths, sacks, etc. Removal of refractory barium-aluminous cement from the mold can take place after 12 to 16 hr.

Following removal, however, the concrete should be kept wet for another two days.

The Resultant Concretes and Their Technical Properties

Using refractory barium-aluminous cement I in the proportions of 10, 15, and 20 percent and white sintered bauxite or wastes of fire clay, corundum, chrome-magnesite, or magnesite bricks in proportions of 90, 85, and 80 percent with given grading, various concrete cubes and prisms were prepared by tamping in metal and wood molds. The more important technical properties of these refractory and highly refractory concretes are given in table 7.

Table 7 shows that the cold compressive strength of concrete increases with increasing cement content and that it is higher after burning at 1,400 °C than prior to such burning. Furthermore one can see that the refractoriness of the concrete decreases with increasing cement content. The resistance of concrete to thermal shock is always higher than that of the corresponding refractory brick. The properties of refractory concrete depend first on the aggregates used and, second, on the cement serving as binder. They are particularly determined by the chemical reactions taking place at high temperatures between the aggregates and the cementing materials. By using suitable refractory aggregates one can prevent the formation of readily fusing ceramic compounds which reduce the refractoriness of the concrete.

Using barium-aluminous cement II in proportions of 10, 15, and 20 percent and wastes of fire brick or white sintered bauxite in the proportions of 90, 85, and 80 percent with identical grading, six types of refractory concrete were prepared whose properties are given in table 8.

To establish the effect of the cements used as binders on the properties of concrete we used 20 percent of portland cement, ordinary aluminous cement (ciment fondu), white aluminous cement

Table 7. *Properties of refractory and highly refractory concrete made with refractory barium-aluminous cement I*

Technological properties	Refractory and highly refractory concrete made with refractory barium-aluminous cement I														
	Fire-clay concretes			Bauxite concretes			Corundum concretes			Chrome-magnesite concretes			Magnesite concretes		
Cement content ... *Percent*	10	15	20	10	15	20	10	15	20	10	15	20	10	15	20
Refractoriness ... *°C*	1, 745	1, 740	1, 730	1, 825	1, 810	1, 790	1, 910	1, 880	1, 865	1, 960	1, 930	1, 880	1, 980	1, 950	1, 920
Seger cone collapse	33/34	33/34	33	37	36/37	36	39/40	39	38/39	41	40/41	39	41/42	40/41	40
Cold compressive strength at 7 days:															
Before burning ... *kg/cm²*	118	124	151	159	171	206	175	189	208	184	200	230	198	205	240
After burning at 1,400 °C ... *kg/cm²*	223	232	279	203	208	234	186	200	214	290	330	345	253	272	324
Apparent porosity:															
Before burning ... *Percent*	24	24	23	21	20	20	18	18	19	22	21	21	19	19	18
After burning at:															
1,200 °C ... *do*	24	23	23	21	21	21	19	20	20	23	22	22	20	20	19
1,400 °C ... *do*	23	23	22	20	20	19	18	19	20	22	20	20	19	18	18
Shrinkage, burning temperature:															
1,200 °C ... *do*	0. 3	0. 5	0. 6	0. 4	0. 5	0. 6	0. 5	0. 6	0. 7	0. 7	0. 8	0. 9	0. 6	0. 7	0. 8
1,400 °C ... *do*	0. 5	0. 6	0. 8	0. 5	0. 7	0. 8	0. 6	0. 7	0. 8	0. 8	0. 9	1. 1	0. 8	0. 8	0. 9
Resistance to thermal shock ... *cycles*	67	79	86	54	64	70	25	33	35	11	13	13	8	9	10

with monocalcium aluminate base, refractory aluminous cement with calcium dialuminate base, refractory barium-aluminous cement I, or refractory barium-aluminous cement (II) to produce six each fire-clay (schamotte) concretes, bauxite concretes, and chrome-magnesite concretes under identical conditions.

The refractoriness and resistance to thermal shock of fire-clay concrete are given in table 9.

Similarly, the refractoriness and resistance to thermal shock of bauxite concretes prepared with different cements are given in table 10.

Table 11 shows the technical properties of chrome-magnesite concrete obtained with different cements as follows: refractoriness, cold compressive strength (at 7 days, before and after burning at 1400 °C), apparent porosity (before and after burning at 1200 and 1400 °C) and resistance to thermal shock.

Table 8. *Properties of refractory and highly refractory concrete made with refractory barium-aluminous cement II*

Technological properties	Refractory and highly refractory concrete made with refractory barium-aluminous cement II					
	Fire-clay concretes			Bauxite concretes		
Cement content ... *percent*	10	15	20	10	15	20
Refractoriness ... *°C*	1, 690	1, 690	1, 670	1, 790	1, 770	1, 750
Seger cone collapse	31	31	30	36	35	34
Cold compressive strength at 7 days:						
Before burning ... *kg/cm²*	120	128	155	161	174	203
After burning at 1,400 °C *kg/cm²*	283	317	435	283	348	337
Apparent porosity:						
Before burning ... *percent*	24	23	23	21	21	20
After burning at						
1,200 °C ... do	25	24	24	22	20	21
1,400 °C ... do	23	22	22	20	19	19
Shrinkage, burning temperature:						
1,200 °C ... do	0. 4	0. 5	0. 6	0. 4	0. 5	0. 6
1,400 °C ... do	0. 6	0. 7	0. 8	0. 6	0. 8	0. 8
Resistance to thermal shock *cycles*	61	69	76	53	63	62

Table 9. *Properties of fire-clay concretes made with different cements*

Technological properties	Fire-clay concrete with 20 percent					
	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness ... *°C*	1, 380	1, 435	1, 530	1, 630	1, 730	1, 670
Seger cone collapse	13	15	20	28	33	33
Resistance to thermal shock ... *cycles*	65	72	79	88	88	83

Table 10. *Properties of bauxite concretes made with different cements*

Technological properties	Bauxite concrete with 20 percent					
	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness ... *°C*	1, 450	1, 500	1, 610	1, 690	1, 790	1, 750
Seger cone collapse	15/16	18	27	31	36	34
Resistance to thermal shock ... *cycles*	47	45	51	54	70	60

TABLE 11. *Properties of chrome-magnesite concretes made with different cements*

Technological properties	Chrome-magnesite concrete with 20%:					
	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium di-aluminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness °*C*	1,520	1,560	1,710	1,810	1,880	1,850
Seger cone collapse	19	20/26	32	36/37	39	38
Cold compressive strength at 7 days:						
Before burning *kg/cm²*	123	215	219	176	230	221
After burning at 1,400 °C *kg/cm²*	481	437	368	333	345	358
Apparent porosity:						
Before burning *percent*	23	23	22	22	21	21
After burning at:						
1,200 °C *do*	20	20	21	22	22	21
1,400 °C *do*	15	16	19	20	20	20
Shrinkage, burning temperature:						
1,200 °C *do*	1.4	1.2	0.8	0.9	0.9	0.9
1,400 °C *do*	------	------	1.2	1.2	1.1	1.1
Resistance to thermal shock *cycles*	9	9	10	11	13	13

The effect of different cements on refractoriness (Seger-cone collapse point) of fire-clay, bauxite, and chrome-magnesite concretes is shown in figure 5 (cement content 20 percent; identical grading and degree of compaction; identical consistancy of concrete.)

Dehydration and Sintering of Refractory Concrete

In general the behavior of concretes shown in table 7 is the same under prolonged heating to 1,500 °C. Up to 105 °C, 40 and 50 percent of the mix water is driven off; up to 300 °C more than 50 percent, and at 900 °C more than 85 percent.

The initial development of the "ceramic bond" between particles of refractory aggregates was observed by means of a binocular (stereoscopic) magnifier.

The various refractory concretes were first exposed to burning temperatures of 800, 900, 1,000, 1,100, 1,200, 1,300, and 1,400 °C for six hours. In the case of chrome-magnesite concretes the "ceramic reaction" begins at about 900 °C, in fire-clay, bauxite, and magnesite concretes at about 1,000 °C, and in corundum concrete first at about 1,100 °C.

The progress of the pyrogenic chemical reactions between the dehydration products of cement and the fine particles of the aggregates can be easily detected in concretes burned at 1,200 °C. The finest particles of the refractory aggregate have almost entirely disappeared and in place of them are very fine voids. These fine voids (small pores) partially disappear at 1,300 °C and completely at 1,400 °C. At this temperature, the particles of aggregate are surrounded with liquid, which forms a glassy, strengthening mass upon cooling. This "ceramic mass" is the cause of "ceramic strengthening," i.e., of the high mechanical cold strengths of refractory concretes burned above 1,300 °C.

The Effect of High Temperature on the Dehydration of Refractory Concrete

The dehydration behavior of fire-clay, bauxite, chrome-magnesite, and magnesite concretes containing 20 percent refractory barium-aluminous cement I under the action of high temperatures up to 1,400 °C was tested on 250-g specimens.

Figure 6 shows that maximum water loss in concrete takes place below 105 °C. At 500 °C fire-clay concrete shows the maximum dehydration. It is followed by chrome-magnesite, bauxite, and magnesite concrete. The higher the apparent porosity of the refractory aggregate, the more readily does dehydration of refractory concrete take place at this temperature.

Effect of High Temperatures on the Cold Compressive Strength of Refractory Concrete

The effect of burning temperatures up to 1,400 °C on the compressive strength at room temperature of fire-clay, bauxite, chrome-magnesite, and magnesite concrete with 20 percent of barium-aluminous cement I was determined.

The compressive strengths of unburned specimens at 28 days were taken as a basis for comparison (100 percent). The cold compressive strength of concrete determined after six-hour heating to different temperatures between 100 and 1,400 °C is shown in figure 7, expressed in percent.

The cold compressive strengths of all concretes increase slightly up to 105 °C, decrease strongly thereafter to 300 °C, and less strongly up to 800–1,000 °C. Upon reaching a minimum, the cold compressive strengths begin to increase very sharply, and, for heating at 1,400 °C, they exceed the original compressive strengths. The diagram shows that due to the pyrogenic chemical reactions in the solid state between the dehydrated components of refractory barium-aluminous cement and the fine sizes of aggregates, a ceramic strengthening of the refractory aggregate particles begins to take place at about 750 °C for chrome-

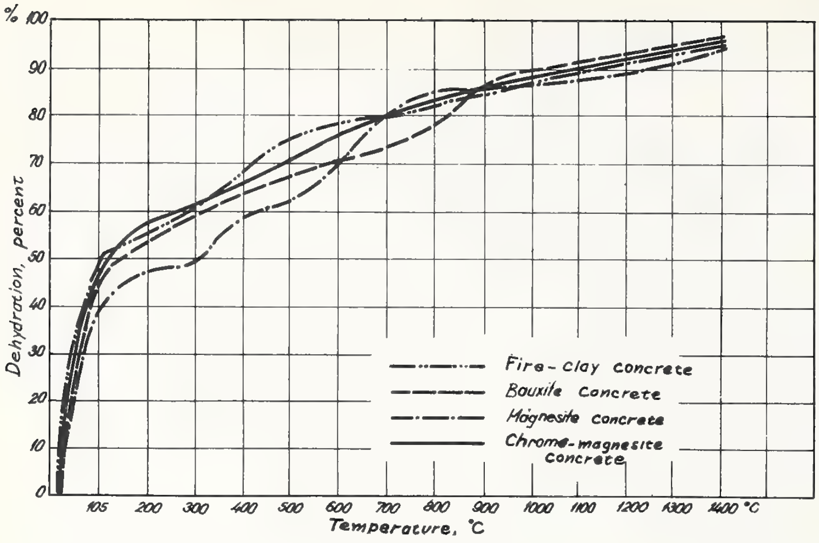

FIGURE 6. *Percent dehydration of fire-clay, bauxite, magnesite, and chrome-magnesite concrete with 20 percent refractory barium-aluminous cement I, for different burning temperatures.*

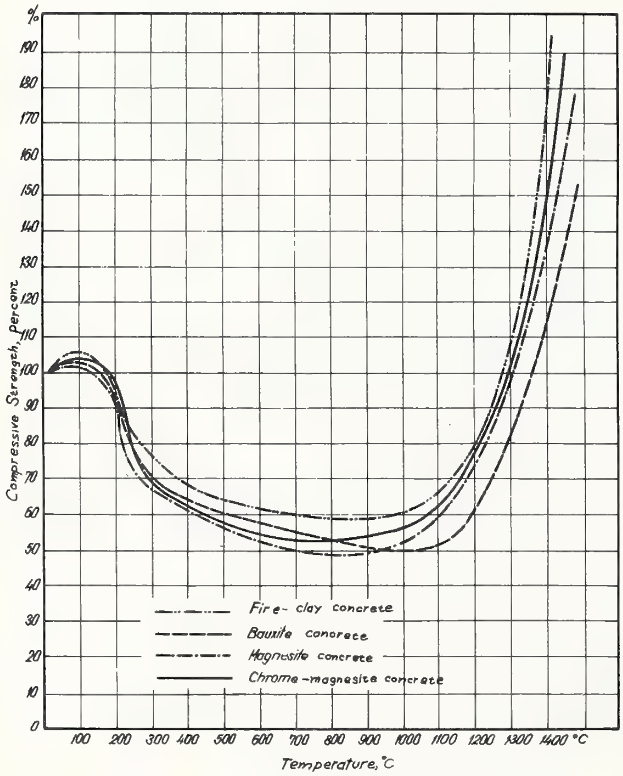

FIGURE 7. *Cold compressive strengths of fire-clay, bauxite, magnesite, and chrome-magnesite concrete with 20 percent refractory barium-aluminous cement I, following six-hour heating to different temperatures.*

magnesite concrete; at about 800 °C for magnesite concrete; at 900 °C for fire-clay concrete, and at 1,000 °C for bauxite concrete.

Following six-hour burning at 1,400 °C the cold compressive strengths exceed the original compressive strengths of unburned concretes.

Effect of Cement Content on the Cold Compressive Strengths of Refractory Concretes

The relation to cement content of the cold compressive strengths (at 7 days) of unburned concretes and those burned at 1,000° or 1,400 °C was studied on fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes, with refractory barium-aluminous cement I. The results for the unburned concretes are reproduced in figure 8, those for concretes burned at 1,000 °C in figure 9, and those burned at 1,400 °C in figure 10.

Figure 8 shows that the compressive strengths of unburned refractory concretes depend to a certain extent on the average compressive strengths of their refractory aggregates. See table 5.

The compressive strengths of refractory concretes increase in general with increasing cement content.

Due to the inhomogeneity of refractory concretes, produced by the settlement of suspended cement particles [25], as well as by the more rapid settlement of the coarser aggregate particles with respect to the smaller, the gain in compressive strength is not uniform.

The effect of cement content on the cold compressive strengths of fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes with barium-aluminous cement I at the so-called "critical point" (burning temperature giving lowest strengths = 1,000 °C) is shown in figure 9. Compared to figure 8, the curves shown here are somewhat flatter. The effect of cement content on the increase in cold compressive strength of concretes is thus smaller at the "critical point."

The effect of cement content on the cold compressive strength of concretes after six-hour burning at 1,400 °C (burning temperature at which "ceramic strengthening" has been in effect for some time) is shown in figure 10. Compared to

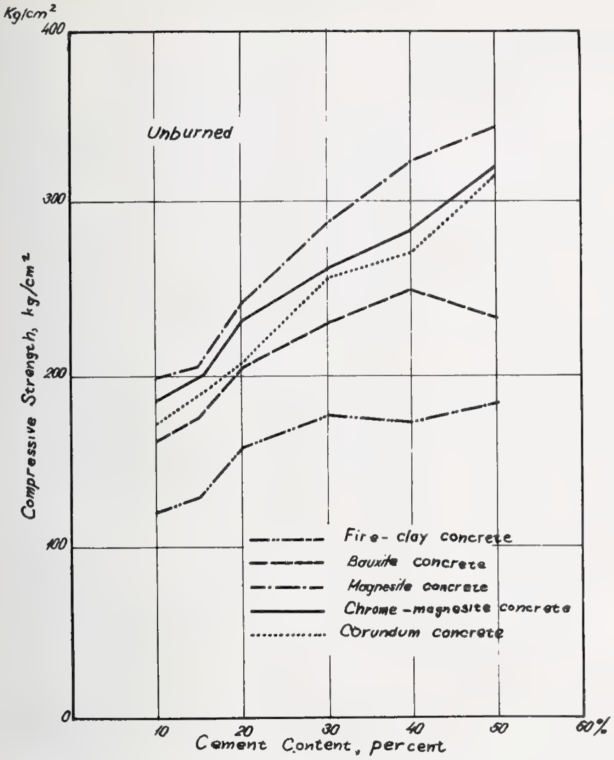

FIGURE 8. *Relation of compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I, unburned, 7 days after setting.*

figure 9, the trend of the curve is considerably steeper. In this case the cold compressive strengths of concretes increase much more markedly with increasing cement content. The cement content thus has a relatively low effect on the cold compressive strength of concrete at the "critical point" and a much more marked effect on the cold compressive strength of unburned refractory concrete or that burned at 1,400 °C.

Relation of Collapse Point of Seger Cone to Cement Content of Refractory Concrete

The effect of cement content on the refractoriness of fireclay, bauxite, corundum, chrome-magnesite, and magnesite concretes with refractory barium-aluminous cement I is shown in figure 11 and table 12.

Table 12 and figure 11 show that in all cases refractoriness decreases with increasing cement content. The drop in refractoriness with increase in cement content from 10 to 30 percent is more marked than for an increase from 40 to 50 percent.

In spite of the greater drop in refractoriness of the magnesite- and chrome-magnesite concretes, the refractoriness of these concretes remains above that of the bauxite and fire-clay concretes.

An increase in cement content has a very pronounced effect on the drop in refractoriness of magnesite and chrome-magnesite concretes and a much smaller effect on the drop in refractoriness of corundum, bauxite, and fire-clay concretes.

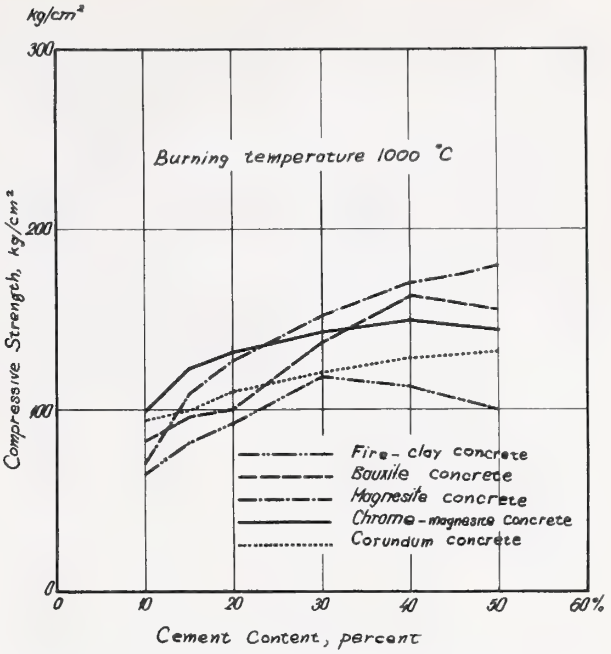

FIGURE 9. *Relation of cold compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I and burned at 1,000 °C at 7 days after setting.*

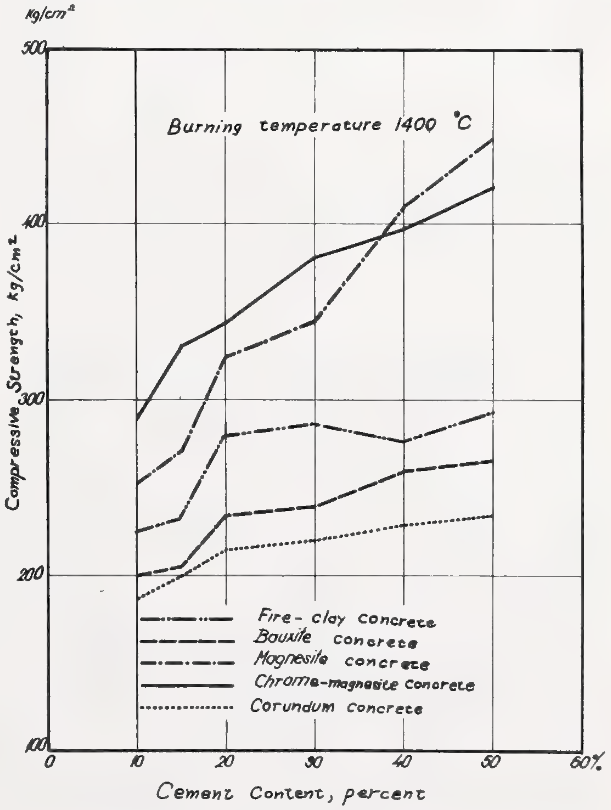

FIGURE 10. *Relation of cold compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with barium-aluminous cement I and burned at 1,400 °C at 7 days after setting.*

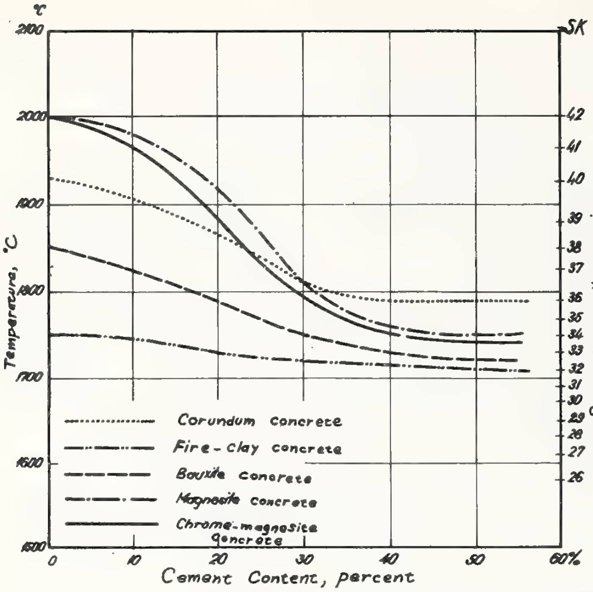

FIGURE 11. *Relation of refractoriness to cement content. in fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I.*

TABLE 12. *Refractoriness of concretes made with different amounts of barium-aluminous cement I*

Cement content	Refractory concrete				
	Fire-clay concrete	Bauxite concrete	Corundum concrete	Chrome-magnesite concrete	Magnesite concrete
Percent	°*C*	°*C*	°*C*	°*C*	°*C*
0	1,750	1,850	1,930	2,000	2,000
10	1,745	1,825	1,910	1,960	1,980
20	1,730	1,790	1,865	1,880	1,920
30	1,720	1,750	1,810	1,790	1,810
40	1,715	1,730	1,790	1,750	1,760
50	1,710	1,720	1,790	1,740	1,750

Seger Cone Collapse Point of Highly Refractory and Refractory Concretes With Barium-Aluminous Cement I and Those With Refractory Calcium-Aluminous Cement With Calcium Dialuminate Base as Related to Increasing Cement Content

The superiority of refractory barium-aluminous cements I and II with respect to the outstanding, widely used refractory aluminous cement with calcium dialuminate base is revealed in figure 12 even more clearly than in figure 5.

The magnesite, chrome-magnesite, corundum, bauxite, and fire-clay concretes were mixed with indentical grading (50 percent coarse, 10 percent medium, and 40 percent fines below 0.2 mm) to identical plastic consistencies and were molded with an identical degree of compaction.

The porosity of highly refractory and refractory concretes with increasing cement content (10 to 40 percent) is 15 to 25 percent higher than the porosity of the aggregates used. It follows—and this has been proved experimentally—that the concretes have lower heat conductivity and higher resistance to thermal shock than the corresponding aggregates, or refractory structural materials, from which they are derived.

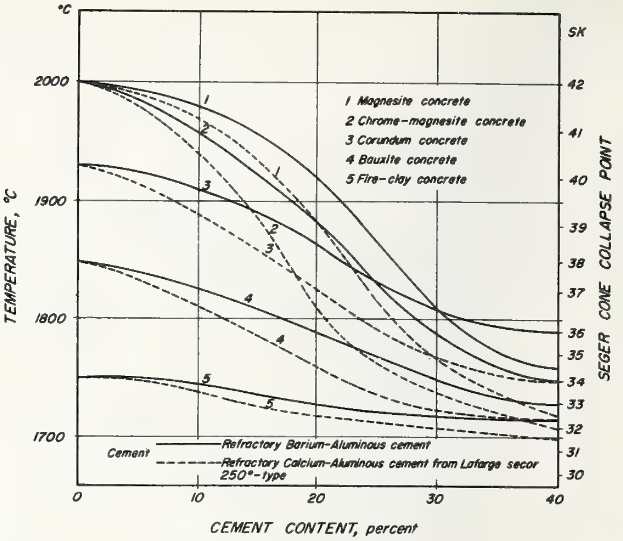

FIGURE 12. *Comparison of refractoriness of magnesite, chrome-magnesite, corundum, bauxite, and fire-clay concretes made with refractory barium-aluminous cement I and refractory calcium aluminous cement with calcium dialuminate base in relation to increasing cement content.*

Figure 12 shows that with a usual cement content of 20 percent the refractoriness of basic highly refractory concretes (magnesite, chrome-magnesite, and corundum concretes) with refractory barium-aluminous cement is 35 to 70 percent higher than that of the corresponding concretes made with refractory aluminous cement with a calcium dialuminate base.

The difference in refractoriness under load is, however, considerably greater for these concretes and indicates the superiority of concrete with refractory barium-aluminous cement.

Thus it is very advantageous, particularly with basic higher refractory concretes, to replace the refractory *calcium-aluminous* cements by refractory *barium-aluminous* cements.

Conclusions

1. From refractory and highly refractory aggregates and portland cement (with finely ground admixtures) only low-grade nonrefractory concretes can be produced which cannot withstand service temperatures above 1,520 °C, when the usual cement content of 20 percent is used.

2. Silicate cements are not suitable for the manufacture of refractory and highly refractory concretes; only aluminate cements, such as refractory barium- and calcium-aluminous cements, should be used. In these the combined water is driven off easily and uniformly at high temperatures without causing destruction of the concrete structure.

3. Conventional aluminous cements with high iron oxide content combined with refractory and highly refractory aggregates produce good, nonrefractory concretes for service temperatures below 1,580 °C.

4. White calcium-aluminous cements with monocalcium aluminate base yield good, refractory concretes only when combined with suitable highly refractory aggregates.

5. Refractory calcium-aluminous cements (with calcium dialuminate base) and refractory barium-aluminous cements yield highly refractory concretes when combined with any basic or neutral refractory aggregates.

6. Highly refractory concretes can be produced only from highly refractory basic neutral aggregates and refractory barium-aluminous cements or refractory calcium-aluminous cements with calcium dialuminate base (with more than 70% Al_2O_3 and less than 1% $Fe_2O_3+SiO_2+MgO+$ alkalies). Of these highly refractory concretes, those containing refractory barium-aluminous cements exhibit the best properties.

7. The thermal shock resistance of concrete depends on the nature of the aggregates, the particle-size gradation, and the quantity of cement. This resistance is considerably higher than that of the corresponding refractory aggregates.

The highest resistance to thermal shock is shown by concretes with barium-aluminous cement. In decreasing order we have: concretes with refractory calcium-aluminous cement with calcium dialuminate base; white aluminous cement with monocalcium-aluminate base; and ordinary (conventional) aluminous cement (ciment fondu). The lowest resistance to thermal shock is shown by portland cement concrete.

Exceptionally high resistance to thermal shock is shown as a rule by fire-clay concretes. These are followed by bauxite, corundum and chrome-magnesite concretes. The lowest resistance to thermal shock is shown by magnesite concretes.

The progress of destruction caused by a severe thermal shock is quite different in the investigated concretes and in the corresponding refractory aggregates. Namely, we deal here with a fine-scale collapse of the concrete rather than with a breaking off of large sections as in refractory brick; this difference is due to the considerably greater inhomogeneity of the concrete.

8. The refractoriness of concrete drops, and its compressive strength increases with increasing cement content. After burning at temperatures of about 1,400 °C the cold compressive strengths of concrete exceed the compressive strengths of unburned concretes (at 7 days).

9. By using barium-aluminous cement as cementing material in combination with basic or neutral aggregates, one can produce refractory and highly refractory concretes, which are superior to those containing refractory calcium-aluminous cements, white aluminous cements, conventional aluminous cements (ciments fondus), or portland cements.

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Paper VIII–S6. Researches on the Hydration of Trass Cements*

U. Ludwig and H. E. Schwiete

Synopsis

The compositions of various Rhenish and Bavarian trasses were investigated chemically and mineralogically. It was found that considerable differences exist between the chemical as well as mineralogical constitutions of Rhenish and Bavarian trasses. The author explains the hydraulic activity of trass by its glassy matrix (groundmass). It was possible to establish that Bavarian trasses have a somewhat higher glass fraction than the Rhenish trasses. The higher hydraulicity of the Rhenish trasses is ascribed to the higher reactivity of the glassy phase of this trass.

The reaction of trass with lime was investigated by shaking trass with lime and water in excess, and also by studies on trass-lime pats, trass-lime suspensions, and trass-cement mortars. Besides this, the lime-combining capacities of the various mineral components of trass were studied. By means of heavy liquids it was also sought to separate the glass phase from the other mineral components, and to test the glass phase for reactivity with lime. On the basis of these tests it can be asserted that over 80 percent of the lime reaction in trass occurs through the glass phases.

With the help of microscopic, electron microscopic, X-ray, and thermal methods of investigation, it was sought to identify the new products formed in a trass-lime reaction. It was shown that the same hydrates form in the system trass-lime-gypsum-water as those familiar in the system portland cement-water. The following hydrates were observed:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$(ettringite), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Résumé

Des recherches chimiques et minéralogiques ont été faites sur la composition de différents trass Rhénans et Bavarois. On trouva que des différences considérables existent entre les constitutions chimiques aussi bien que minéralogiques des trass Rhénans et Bavarois. L'auteur explique l'activité hydraulique du trass par sa gangue vitreuse (milieu de base). Il fut possible d'établir que les trass Bavarois ont une fraction de verre quelque peu plus élevée que les trass Rhénans. L'activité hydraulique supérieure des trass Rhénans est attribuée à la réactivité plus élevée de la phase vitreuse de ce trass.

On examina tout particulièrement la réaction du trass avec la chaux. L'étude de la réaction du trass avec la chaux fut faite en agitant du trass avec de la chaux et de l'eau en excès, et on fit aussi des études sur des mottes de chaux et de trass, des suspensions de chaux et de trass, et des mortiers de ciment et de trass. En outre, les capacités des différents composés minéraux du trass à se combiner à la chaux furent étudiées. Au moyen de liquides lourds on chercha aussi à séparer la phase vitreuse des autres composants minéraux, et à éprouver la phase vitreuse quant à la réactivité avec la chaux. Sur la base de ces expériences on peut affirmer que plus de 80% de la réaction de la chaux dans le trass se produit dans les phases vitreuses.

A l'aide de méthodes de recherches microscopiques, electron microscopiques, de rayons X et thermiques, on chercha à identifier les nouveaux produits formés dans la réaction trass-chaux. On trouva que les hydrates qui se forment dans le système trass-chaux-gypse-eau sont les mêmes que ceux trouvés ordinairement dans le système ciment portland-eau. Ce qui signifie que les hydrates suivants ont été observés:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (ettringite), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Zusammenfassung

Verschiedene rheinische und bayrische Trasse wurden chemisch und mineralogisch auf ihre Zusammensetzung untersucht. Dabei ergab sich, daß zwischen dem chemischen und auch mineralogischen Aufbau der rheinischen und bayrischen Trasse wesentliche Unterschiede bestehen. Die Verfasser erklären die hydraulische Wirksamkeit der Trasse durch die glasige Grundmasse. Es konnte festgestellt werden, daß in den bayrischen Trassen ein etwas höherer Glasanteil enthalten ist als in den rheinischen Trassen. Die höhere Hydraulizität der rheinischen Trasse wird auf ein größeres Reaktionsvermögen der Glasphase dieses Trasses zurückgeführt.

Der Kalkbindung der Trasse wurde besondere Aufmerksamkeit gewidmet. Es wurde die Kalkbindung beim Schütteln von Traß mit Kalk und Wasser im überschuß, an Traßkalkkuchen, an Traßzement-Suspensionen und an Traßzement-Mörteln untersucht. Außerdem wurde zusätzlich das Kalkbindungsvermögen der verschiedenen am Aufbau der

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Trasse beteiligten Mineralien ermittelt. Zusätzlich wurde versucht, mit Hilfe schwerer Flüssigkeiten die Glasphase der Trasse von den übrigen Mineralkomponenten abzutrennen und diese auf ihr Kalkbindungsvermögen zu prüfen. Anhand dieser Versuche konnte nachgewiesen werden, daß über 80% der Kalkbindung der Trasse durch die Glasphasen erfolgt.

Mit Hilfe mikroskopischer, elektronenmikroskopischer, röntgenographischer und thermischer Untersuchungsmethoden wurde versucht, die bei dem Umsatz von Traß mit Kalk entstehenden Neubildungen zu identifizieren. Dabei zeigte es sich, daß im System Traß-Kalk-Gips-Wasser die gleichen Hydrate gebildet wurden, wie sie uns vom System Portlandzement-Wasser bekannt sind. Das heißt, es wurden folgende Hydrate beobachtet:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (Ettringit), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Introduction

Geologically, trass is a volcanic tuff; from the standpoint of building technology it is a hydraulic admixture which hardens hydraulically in combination with lime and water. Because of its ability to harden hydraulically, trass has been used in construction for centuries.

In Germany, trass deposits used industrially are found in the Eifel and in Nördlinger Ries. Other deposits occur in the Rhön and in Saxony.

The subject matter treated below is divided into three parts:

(a) the chemical and mineralogical composition of trass,

(b) the binding of lime by trass, and

(c) products formed during hydration of trass in the presence of lime.

Properties which trass imparts to mortar from the engineering standpoint will not be discussed in this paper, although numerous strength tests and measurements of workability and of water repellence in mortar were made.

Results of Investigations

The Chemical and Mineralogical Composition of Trass

Table 1 presents analytical results obtained in standard tests on Rhenish trass. In this analytical method the trass samples are boiled with 20 percent HCl for 1 hr with reflux condenser. The residue is then treated with 2-percent NaOH solution.

Table 2 presents results of standard analyses obtained with several kinds of Bavarian trass. These results differ from those for Rhenish trass in that Rhenish trass has an HCl-insoluble residue of 30–46 percent, while that for Bavarian trass is about 50–60 percent. On the other hand, Rhenish trass contains more alkalies and more water of hydration.

However, for explaining the action of trass, the chemical analyses and contents of individual oxides are not decisive, but instead the nature of the chemical binding of the oxides in trass glass and trass minerals. For this reason, up to about the middle thirties, attempts to explain the mineralogical structure of trass were based on combined chemical and microscopic methods. Of the many researchers, we mention the following: Hambloch [1], Hart [2], Lunge [3], Biehl and Wittekindt [4] and Tännhäuser [5].

Greatest care was taken in the present studies in determining the mineral composition of trass.

TABLE 1. *Chemical analyses of Rhenish trass*
(In accordance with DIN 1044)
[Percent]

Sample No.	1	2	3	4	5	6	7	8	9
Sample [a]	Ta$_H$	Tu$_H$	Ti$_H$	Ta$_J$	Tu$_J$	Ob$_T$	Un$_T$	Rö$_K$	Fr$_K$
Loss on ignition	4.62	11.36	9.40	6.30	9.92	11.10	11.84	8.10	7.24
Insoluble	32.28	30.08	44.32	46.12	33.48	33.56	26.40	31.40	32.36
SiO_2	31.84	33.18	25.02	25.82	30.78	29.56	32.74	34.98	35.18
Fe_2O_3	4.12	3.48	3.87	3.87	3.87	4.38	4.27	2.94	3.13
Al_2O_3	15.18	14.00	9.63	10.75	12.41	13.54	14.05	14.10	13.39
CaO	2.52	3.34	3.09	2.10	3.33	3.30	2.71	2.29	1.80
MgO	1.22	.82	.76	1.04	1.10	1.00	1.05	.75	.65
SO_3 [b]	.04	Sp	Sp	Sp	Sp	Sp	Sp	.02	Sp
Mech. water	.92	4.02	2.20	1.16	4.88	4.11	4.05	2.71	1.46
Water of hydration	3.73	7.64	7.36	5.20	5.63	7.28	8.11	5.63	5.68
Total	91.82	96.26	97.09	96.00	95.21	96.44	93.06	94.68	93.75

[a] Trass samples dissolved in HCl.
[b] Sp=trace.

Table 2. *Chemical analyses of Bavarian trass*
(In accordance with DIN 1044)
[Percent]

Sample No.	12 [b]	13	14	15	16	17	18	19	20 [c]
Sample [a]	PC375	Tr_{01}	Tr_{02}	Tr_{03}	Tr_{04}	Tr_H	Tr_A	Tr_M	PC375
Water of hydration	--------	5. 54	3. 24	3. 44	3. 67	3. 10	4. 37	7. 00	--------
Insoluble	0. 17	51. 57	54. 62	58. 09	53. 60	59. 36	52. 73	53. 15	0. 22
SiO_2	20. 92	23. 50	25. 43	22. 10	23. 44	19. 21	23. 62	19. 84	19. 80
Fe_2O_3	2. 69	4. 53	3. 15	3. 80	4. 15	3. 44	3. 79	3. 17	2. 95
Al_2O_3	5. 77	8. 51	6. 86	6. 34	8. 29	6. 59	6. 53	4. 83	6. 86
CaO	65. 90	1. 67	1. 31	2. 39	1. 73	4. 22	3. 53	7. 84	65. 20
MgO	1. 30	1. 89	1. 47	2. 10	1. 84	1. 09	2. 84	1. 21	1. 19
SO_3 [d]	2. 71	. 22	Sp	Sp	. 33	Sp	Sp	Sp	3. 31
Total	99. 46	97. 43	96. 08	98. 26	97. 05	97. 01	97. 41	96. 68	99. 53
Na_2O [e]	. 08	1. 54	1. 38	1. 51	1. 73	1. 91	2. 09	1. 86	. 07
K_2O [e]	. 61	2. 30	2. 53	2. 41	2. 32	2. 44	1. 78	2. 44	. 65

[a] Trass samples dissolved in HCl.
[b] PC 375 No. 12: silicate mod.=2.47; alumina mod.=2.15; hydr. mod.=2.24.
[c] PC 375 No. 20: silicate mod.=2.02; alumina mod.=2.32; hydr. mod.=2.20.
[d] Sp=trace.
[e] Decomposed with hydrofluoric acid.

Samples were subjected to chemical analysis and examined optically and roentgenographically.

A comparison of the results of mineralogical investigations of trass obtained by Völzing [6] and Tannhäuser with those of the authors is presented in table 3. The important differences revealed in this comparison with earlier investigations consist in that recent tests showed greater quantities of quartz and leucite and small quantities of kaolinite and illite in the fine fractions of the prepared trass samples. In addition, the presence of cristobalite is also probable. On the other hand, accessory minerals such as apatite, titanite, hauynite, sodalite, and magnetite were not revealed in the new tests, which fact may be attributed to the rarity of their occurrence and to the different test methods used. Whereas, formerly, the samples were "grab" or random samples, our tests were carried out with average powdered samples. Accessory minerals obtained in our investigations, particularly illite, kaolinite, and chabazite, could not be detected earlier because of their great fineness which made identification with the light microscope impossible.

Table 3. *Mineral components of Rhenish trass*

Accdg. to Völzing (1907) and Tannhäuser (1911)				Authors' tests
Microscope				X-ray diffraction and microscope
	————		quartz	
	feldspar	⟷	feldspar	
	hornblende	⟷	hornblende	
	augite	⟷	augite	
	apatite		—	
	titanite		—	
	biotite	⟷	or muscovite	
	hauynite		chabazite	
	nosean	⟷	analcite	
	sodalite		hematite	
	magnetite		cristobalite	
	—		lecuite	
	—		kaolinite	
	—		illite	
	glass (matrix)	⟷	glass	

Table 4 presents a comparison of the chemical compositions of a Rhenish trass and a Bavarian trass and the compositions of the glass components separated from the two trass samples by means of heavy liquids.

Table 4. *Chemical and mineralogical composition of a Rhenish trass and Bavarian trass*

Chemical composition (%)					Mineralogical composition (%)		
	Rhenish trass		Bavarian trass			Rhenish trass	Bavarian trass
	Trass	Glass	Trass	Glass			
Loss on ignition	11. 10	7. 83	7. 41	5. 15	Glass	55–60	62–67
					Quartz	9	19
SiO_2	52. 12	54. 85	62. 45	67. 14	Feldspar	15	15
Fe_2O_3	5. 81	4. 55	4. 41	1. 95	Chabazite	3	-------
Al_2O_3	------	18. 14	------	15. 34	Analcite	5	-------
	18. 29		16. 47		Leucite	4	-------
TiO_2	------	. 76	------	0. 64	Mica	2	-------
CaO	4. 94	4. 40	3. 39	2. 76	Illite	-------	-------
MgO	1. 20	1. 92	. 94	. 93	Augite	<1	<1
SO_3 [a]	Sp	. 34	Sp	1. 06	Kaolinite	2	-------
Na_2O	1. 48	1. 37	1. 91	2. 02	Hornblende	<1	-------
K_2O	5. 06	5. 48	2. 06	2. 72			

[a] Sp=trace.

The results show that the analyses of trass glass and of the corresponding trass have a certain similarity. The glass in Bavarian trass is more acid and contains less alkalies, particularly less potassium.

The mineralogical compositions of Rhenish and Bavarian trass are quite different. As indicated by table 4, Bavarian trass contains neither zeolites nor leucite, but has a definitely higher quartz content.

Great significance was attributed to the magnitude of the content of water of hydration in the trass. This led to a renewed thorough investigation of the nature of the bonds by which water is held. It was established that only a small part of the chemically bound water is fixed in the crystalline components. The greater part of the water, which cannot be driven off at 110 °C, is fixed in the glassy phase of trass. Infrared spectroscopy studies established that even when trass glass was tempered at 200 °C adsorption water was still present along with chemically bound water. These results show that the importance of the water of hydration in trass with respect to the capacity for hydraulic hardening requires further verification.

The Binding of Lime by Trass

It is known that the trass component in trass cement reacts with the lime liberated during the hydration and hydrolysis. Consequently, trass-lime tests were given special attention in the present series. The degree of trass-lime reaction was studied on: (a) trass-lime suspensions, (b) trass-lime pats, (c) trass-cement suspensions, (d) trass-cement mortars. The test reactions extended over a period of 2 yrs. The free lime present as uncombined $Ca(OH)_2$ or, in mortars, partly as $CaCO_3$ was determined by the modified Franke method and gas volumetrically. The free lime going into solution in shaking tests was determined, together with the alkalies, by flame photometry. The investigated trass samples had a specific surface of 8,000–9,000 cm^2/g.

Figure 1 shows the lime binding of a Rhenish trass shaken up to 660 days in a lime suspension. Plotted as ordinates are: (a) CaO combined with trass, (b) free lime present in the solution and in the solids, (c) free alkalies present in the solution in mg/g trass. The abscissa shows the logarithm of time.

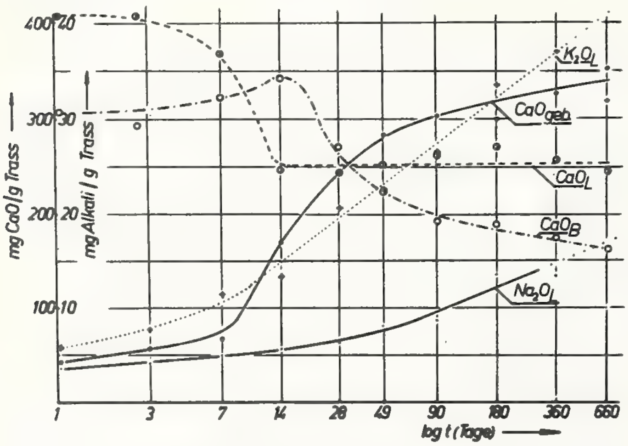

FIGURE 1. *Alkali separation and lime fixation of a Rhenish trass.*

CaO_{geb}=combined lime; CaO_B=free lime; other curves refer to amounts in solution; abscissa=time in days on log scale.

The diagram reveals an increasing solubility of alkalies. Strong lime supersaturation was first observed in the solution, which dropped to saturation concentration after 14 days. On the other hand, the free lime content in the solids at first increases, reaches a maximum after 14 days and drops thereafter, in accordance with the strong reaction of trass with lime. This gives a hyperbolically-shaped curve extending down to about 160 mg in the solids.

The S-shaped trend of the lime reaction curve can be explained by an initial lime adsorption which may be overlain by ion-exchange reactions (resulting from the zeolite content of trass), and a reaction beginning at 7 days (appearance of new formations) which after about 49 days passes into a period of lime saturation of the solids.

It should be mentioned at this point that alkali loss and lime fixation do not exhibit a proportional relation, i.e., that the extent of the lime reaction is to be explained not only through zeolitic reactions, but almost exclusively through chemical conversion reactions, which is confirmed by the observed new formations.

In an attempt to define the participation of the individual trass components in the lime reaction, several minerals, namely, quartz, feldspar, leucite, kaolinite, and analcite, and (in addition) obsidian were ground to ultrafineness, and their reactivity with lime was examined as for trass. The duration of the reaction was 28 days. Besides these, glassy phases of various specimens of Rhenish and Bavarian trass were separated from the crystalline phases by means of heavy liquids, and the ability of these glasses to react with lime was investigated. The results of these investigations are presented in table 5. An evaluation of the investigations shows that more than 80 percent of the lime reaction takes place through the glass phase. A study of Bavarian trass led to the same results.

TABLE 5. *The lime-binding capabilities of the principal trass minerals and their contributions to trass-lime binding*

Mineral component	Lime reaction	Free alkali		Average amount in Rhenish trass	Calculated lime reaction in Rhenish trass
		Na_2O	K_2O		
	mgCaO/g	*mg/g*	*mg/g*	*percent*	*mgCaO/g trass*
Quartz	43	1.5	0.4	13	5.6
Feldspar	117	1.1	.2	15	17.5
Leucite	90	1.3	1.8	6	5.4
Analcite	190	10.7	3.0	7	13.3
Kaolin	34	.3	2.1	2	.7
Glass phase (Rhenish)	364	18.0	24.0	55	200.0
Glass phase (Bavarian)	272	6.0	6.0	66	179.0
Obsidian glass	176	3.7	3.1		
Total				98	242.5

From the table the following can be deduced: The increasing fixation of lime in the series obsidian glass→trass glass (Bavarian)→trass glass (Rhenish), and the quantities of liberated alkalies increasing in the same order could be an indication that the reactivity of the glasses depends on the level of the alkali content, a view, however which needs the support of further studies.

In studies of trass-lime pats, the bound lime was determined after 360 days as 309 mg CaO or 408 mg $Ca(OH)_2$ per g trass. Table 6 presents the results obtained in these studies.

By shaking portland cement, trass cement, and "quartz cement" with an excess of water, the lime fixation of the Rhenish trass under study was established at the same level as in the earlier tests. In addition, the quartz flour used was found to show some reactivity with respect to lime. After a duration of the reaction of 1 yr, lime fixation by trass amounted to 329 mg CaO and that of quartz flour to 73 mg CaO per g trass or quartz, respectively.

TABLE 6. *Fixation of lime by Rhenish trass as a function of time* (W/B=1)

Duration of curing	Free $Ca(OH)_2$	Lime reaction with 1 g trass computed as	
		$Ca(OH)_2$	CaO
Days	*Percent*	*mg*	*mg*
0	50.3	0	0
3	48.7	32	24
7	45.1	104	79
14	39.1	224	170
28	36.4	278	211
92	33.9	328	248
180	33.7	332	252
360	29.9	408	309

The content of free lime found in studies of standard mortars made in accordance with DIN 1164, and the lime fixation calculated therefrom for the different Rhenish trass samples are presented in table 7.

After a 365-day duration of storage the average content of free lime in trass mortars amounts to about 26 mg, that in a portland-cement specimen to 63 mg, and in the comparable mortar specimen with 30 parts quartz flour to 38.2 mg free CaO per g mortar (ignited basis). The lime fixation by trass increases sharply as a function of time and amounts to 24 percent on the average after 1 yr water storage of mortar prisms. In comparison, quartz flour binds 7.9 percent CaO in the same interval.

Products Formed During Hydration of Trass in the Presence of Lime

Available for these investigations, besides the polarizing microscope were: an electron microscope, an X-ray diffraction apparatus, and the dynamic differential calorimeter, an advanced DTA method.

Figure 2 shows the X-ray diffraction charts of the Rhenish trass reacted with lime up to 660 days. It reveals a drop in free lime as a function of time, which is indicated by a decrease in intensity of diffraction lines at $\theta = 9$ and 17°, respectively. These are the principal lines of $Ca(OH)_2$. The basic diffraction lines for the new hydration products lie in the range $\theta = 5–7°$.

TABLE 7. *Lime liberation and lime fixation in standard mortars made according to DIN 1164*

No.	Cement	Free CaO in 1 g mortar				Lime binding by trass or quartz content							
		7d	28d	180d	365d	7d		28d		180d		365d	
		mg	*mg*	*mg*	*mg*	*mg* [a]	% [b]	*mg* [a]	% [b]	*mg* [a]	% [b]	*mg* [a]	% [b]
0	PC375	70.0	69.0	64.5	63.0								
1	30 percent Ta$_{\mathrm{H}}$	45.1	39.7	33.2	27.9	3.9	5.2	8.6	11.4	12.0	16.0	16.2	21.6
2	30 percent Tu$_{\mathrm{H}}$	44.0	35.9	29.0	22.6	5.0	6.7	12.4	16.5	16.2	21.6	21.5	28.6
3	30 percent Ti$_{\mathrm{H}}$	45.3	41.8	34.2	28.6	3.7	4.7	6.5	8.7	11.0	14.6	15.5	20.6
4	30 percent Ta$_{\mathrm{J}}$	43.9	40.2	34.1	27.6	5.1	6.8	10.4	13.8	11.1	14.8	16.5	22.0
5	30 percent Tu$_{\mathrm{J}}$	43.8	37.0	33.0	23.9	5.2	6.9	11.3	15.0	12.2	16.2	20.2	26.9
6	30 percent Ob$_{\mathrm{T}}$	44.3	38.4	32.8	26.5	4.7	6.3	9.9	13.2	12.4	16.5	17.6	23.4
7	30 percent Un$_{\mathrm{T}}$	43.5	38.0	32.3	25.4	5.5	7.3	10.3	13.7	12.9	17.2	18.7	24.9
8	30 percent Rö$_{\mathrm{K}}$	46.9	41.5	31.9	24.8	2.1	2.8	6.8	9.1	13.3	17.7	19.3	25.7
9	30 precent Fr$_{\mathrm{K}}$	45.4	41.0	32.8	26.2	3.6	4.8	7.3	9.7	12.4	16.5	17.8	23.7
10	30 percent quartz	47.3	46.2	41.2	38.2	1.7	2.3	2.1	2.8	4.0	5.3	5.9	7.9

[a] On the basis of 1 g mortar.
[b] On the basis of the trass or quartz content of the mortar.

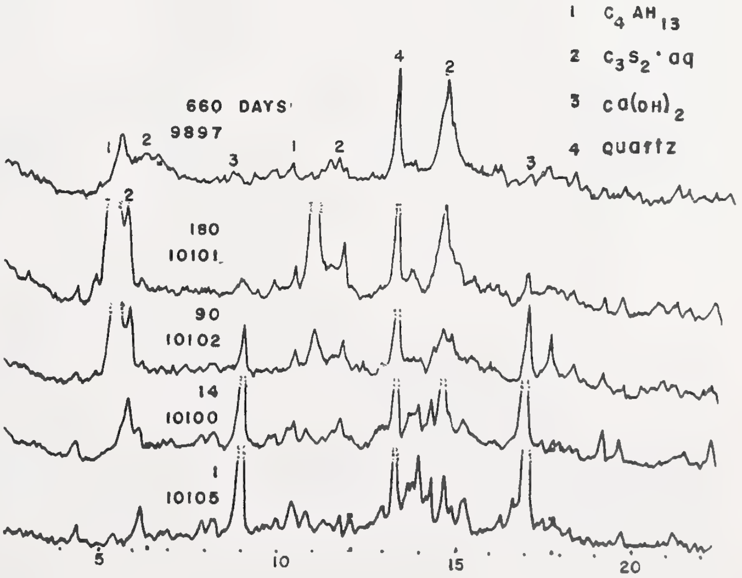

FIGURE 2. *X-ray diffraction patterns of Rhenish trass-lime mixtures shaken for periods up to 660 days.*

From bottom to top: 1 day, 14 days, 90 days, 180 days, 660 days. Abscissa scale, angle θ in degrees.

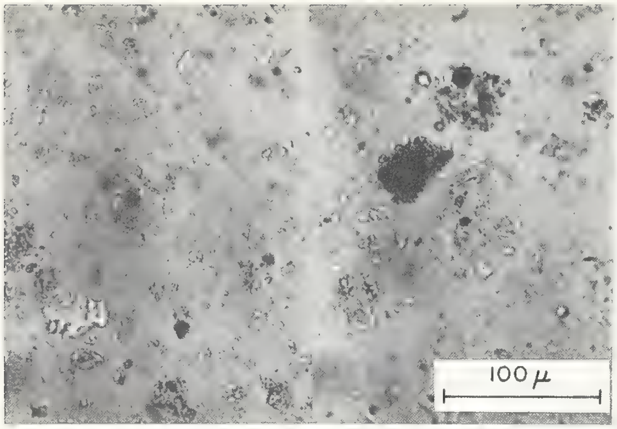

FIGURE 3. *Hydrated products of the reaction of trass with lime (photomicrograph).*

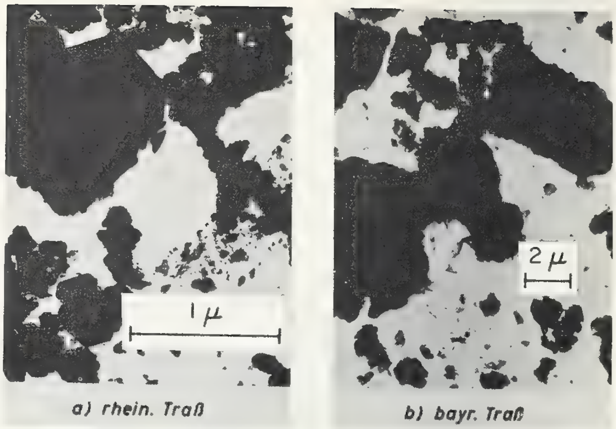

FIGURE 4. *Reaction products obtained by shaking (a) Rhenish trass, (b) Bavarian trass, with limewater (electron micrographs).*

The basic diffraction line of tricalcium disilicate hydrate makes its appearance after 14 days of the reaction, and another new product, C_4AH_{13}, is observed after 28 days, with its characteristic strong diffraction line at 5.3°. The calcium silicate hydrate phase is particularly characterized by a diffraction line at 14.5°.

No final explanation has yet been given for the displacement of the basic diffraction lines after a 660-day duration of the reaction. Specifically, it should be verified whether C_4AH_{13} changes by combining with silica into C_4ASH_{14}, first described by Flint and Wells [7] and later by Dörr [8], which has not as yet been synthesized in pure form.

Figure 3 shows a photomicrograph of hexagonal platelets of C_4AH_{13} formed in the trass-lime reaction.

Figure 4 presents the reaction products of (a) Rhenish trass and (b) Bavarian trass with lime.

In the reacted Rhenish trass are found, along with small hexagonal platelets consisting of C_4AH_{13}, some clearly transparent crystals with conchoidal fracture, which prove to be calcium silicate hydrate. In contrast to this, in the reaction of Bavarian trass with lime, one observes almost exclusively calcium silicate hydrate, which is particularly well revealed at the particle boundaries of the larger trass particles by its transparency and conchoidal fracture.

The observation that less aluminate hydrate forms in the reaction of Bavarian trass with lime than in that of Rhenish trass yields in this test a confirmation of the fact that in the system Rhenish trass-lime-gypsum-water one finds besides the already mentioned new products also ettringite and $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$, which are present only in small degree in the Bavarian trass system.

The systems portland cement-water and trass cement-water yielded the same hydration products as were observed in the gypsum-containing system with Rhenish trass and lime. Marked differences in the X-ray charts are shown only by the contents of free lime While in hydrated trass cement $Ca(OH)_2$ was observed after prolonged shaking only to a small degree, the strong diffraction lines in portland cement indicate large quantities of free lime.

The individual hydrates observed in hydrated portland cement and trass cement were as follows:

$Ca(OH)_2$
$3CaO{\cdot}2SiO_2{\cdot}aq.$
$4CaO{\cdot}Al_2O_3{\cdot}13H_2O$
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (ettringite)
$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Thus our studies show that new products formed during the reaction of trass with lime in aqueous solutions are identical with those formed in the reaction of portland cement or trass cement with water.

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Paper VIII–S–7. High Strength Rapid-Hardening Concrete*

B. G. Skramtaev

Synopsis (By editor)

Methods by which concrete of high early strength is produced in the Soviet Union are briefly presented. These methods are: use of high early strength cement, additional grinding of the cement at the concrete plants, vibration to permit use of low water-cement ratio, use of calcium chloride admixture, conventional steam curing at steam temperatures up to 100 °C, steam curing at 100 °C with the concrete covered by rubber sheeting, high-pressure steam curing in autoclaves, and self-steaming in closed molds at 140–150 °C.

Résumé

Les méthodes selon lesquelles le béton de haute résistance initiale est produit en Union Soviétique sont présentées en bref. Ces méthodes sont les suivantes: l'utilisation de ciment à haute résistance initiale, le broyage supplémentaire du ciment dans les usines de béton, la vibration pour permettre l'usage d'un rapport eau-ciment peu élevé, l'utilisation d'addition de chlorure de calcium, la conservation normale à la vapeur à des températures de vapeur allant jusqu'à 100 °C, la conservation à la vapeur à 100 °C avec le béton sous revêtement de caoutchouc, la conservation à la vapeur sous haute pression dans des autoclaves, et l'auto-traitement par vapeur dans des moules clos à 140–150 °C.

Zusammenfassung

Methoden mit deren Hilfe ein schnellerhärtender hochfestiger Beton in der Sowietunion hergestellt wird, werden kurz besprochen. Diese sind: Benutzung schnellerhärtender Zemente; nochmaliges Mahlen der Zemente in der Betonfabrik; Anwendung eines Rüttlers, sodass man mit einem niedrigen Wasser-Zementverhältnis arbeiten kann; Hinzumischung von Kalziumchlorid; ordinäre Dampfbehandlung bis 100 °C; Behandlung mit 100 °C Dampf, wobei der Beton mit Gummimatten bedeckt wird; Hochdruckdampfbehandlung im Autoklaven, und Selbstdampfentwicklung in verschlossenen Formen bei 140–150 °C.

Each country which produces precast and prestressed concrete has to have high strength rapid-hardening concrete, and therefore uses high-early-strength portland cement, steam curing, or heating of concrete. All three methods are used in the Soviet Union.

Generally we produce portland cement of five types according to its compressive strength after 28 days: 300–400–500–600–700 kg/cm^2. The last three types are used for making precast and prestressed concrete structures.

A part of this cement is high-early-strength portland cement. The demand of our technical specifications for this cement is: compressive strength at the age of 1 day (24 hr) no less than 200 kg/cm^2 (practically it reaches 250, sometimes more), at the age of 3 days no less than 300 kg/cm^2 (practically 350 kg/cm^2 and more).

For the production of high-early-strength portland cement we use a good clinker with the total content of C_3S and C_3A no less than 60 percent, a little higher addition of gypsum (up to 3.5 percent SO_3) and very fine grinding.

Sometimes to accelerate the hardening of cement and obtain fresh cement we use additional grinding of cement at the concrete plants, using the new mills, the so-called vibromills, and adding gypsum up to 6 percent SO_3.

An additional way of obtaining high-strength rapid-hardening concrete is the use of a dry concrete mixture with low water-cement ratio, less than 0.35, and vibration under load or vibropressure.

The next method of producing rapid-hardening concrete is the well-known admixture of calcium chloride, but we use it only for structures with reinforcement steel in diameter not less than 5 mm. The corrosion of steel is dangerous for thin wire.

The properties of rapid-hardening cement and concrete are active only under normal temperature conditions. Due to the severe climate of the larger part of the USSR we have to use very often the steam curing of concrete. In this case there is no necessity to have high-early-strength portland cement.

In the field of steam curing we have such a novelty as the high temperature of steam, up to 100 °C. Some years ago we were afraid of using steam with temperature higher than 70 °C. Now when we use pure wet steam and portland cement with the content of C_3A not higher than 8 percent, we have very good results with steam curing at the temperature up to 100 °C. Because of this we have shortened the period of steam curing down to 8 hr instead of 16 hr. After steam curing we obtain compressive strength not less than 70 percent of normal 28-day strength. This is good enough for the transportation and erection of precast concrete units.

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When we produce the large wall and floor panels by roll machines we use the heating of concrete at the temperature 100 °C, but in this case the concrete is enclosed by a rubber sheet. After 3 hr of this treatment, we have a compressive strength of concrete not less than 200 kg/cm^2.

The most rapid hardening of concrete is under steam-pressure curing in autoclaves or new process-heating in closed molds, so-called self steaming. This process was developed by V. V. Mikhailov in 1937. Using a very dry concrete mixture with w/c=0.25, vibropressure, and heating at the temperature 140–150 °C, he obtained after 2 hr the compressive strength of concrete, 400 kg/cm^2, and after 28 days, 1,000 kg/cm^2.

This is indeed rapid-hardening and high-strength concrete. The process is used for making prestressed pipes.

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